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# TOWARD A NEW THERMOPLASTIC EPOXY-BASED SYSTEM: NANOCOMPOSITE AND FIBRE REINFORCED MATERIAL BY REACTIVE PROCESSING

**Ph.D. Dissertation**

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# ABSTRACT

Thermoplastic composites allows attractive advantages over their thermosetting counterparts like a higher toughness, faster and more flexible manufacturing and an intrinsic recyclability. Thermoplastic composite parts, nevertheless, are limited in size and thickness by traditional melt processing.

As an alternative, reactive processing of textile fibre-reinforced thermoplastics is a very attractive theme. Reactive processing systems stand as the next breakthrough of advanced composite development and materials research investigations due to their inherent synergy between thermoplastic characteristic performance and thermosetting manufacturing processes, representing an high technological hybrid solution for many industrial sectors. The idea of produce an epoxy-based reactive system which exhibit a thermoplastic behavior is not far away, due to consolidated know-how on reactive processing of thermosetting epoxy resins.

In this work, an epoxy-based system which can be reactively processed preserving the advantages of a thermoplastic system was investigated and characterized. Applications in polymer/carbon nanotubes nanocomposites ad fiber reinforced composites were analyzed and focused.

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# 1.

# THERMOPLASTIC COMPOSITES BY REACTIVE PROCESSING

## 1.1 Introduction

Thermoplastic composites allows attractive advantages over their thermosetting counterparts like a higher toughness, faster and more flexible manufacturing and an intrinsic recyclability. Traditional melt processing, however, limits thermoplastic composite parts in size and thickness. As an alternative, reactive processing of textile fibre-reinforced thermoplastics is a very attractive theme: low viscosity mono- or oligomeric precursors are used to impregnate the fibres, followed by in situ polymerization. Great interest in this field is confirmed by interest of some big producers of chemical intermediates, which are developing and patenting[1, 2], new system for different applications. Recently, cost effective solutions based on the concept of reactive processing of a thermoplastic products have been developed and investigated, specially for the automotive industry. Recent developments in reactive thermoplastic technology have enabled consideration of thermoplastic liquid impregnation processes, offering a tougher matrix system with the potential for recycling in the light of up-to-date end of life vehicle regulations. A further fundamental advantage includes the ability to post-form structures after the first moulding step. Verrey et al.[3] compares resin transfer moulding (RTM) processes for automotive body-in-white (BIW) structures, both for thermoset and thermoplastic resins, also from the cost effectiveness point of view. In Figure 1 is shows a monolithic floor-pan which can be produced by reactive processing.

Reactive processing systems stand as the next breakthrough of advanced composite development and materials research investigations due to their inherent synergy between thermoplastic characteristic performance and thermosetting manufacturing processes, representing an high technological hybrid solution for many industrial sectors.

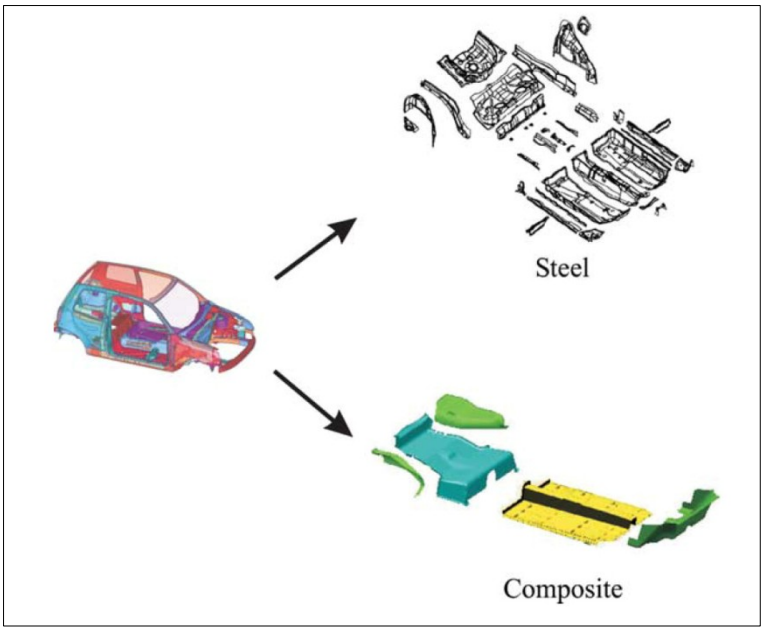


Figure 1 - Monolithic floor-pan to be produced according to the equivalent steel part.[3]

## 1.2 Thermoplastic matrices for composite applications

Thermoplastic composites (TPCs) offer important advantages over thermosetting systems. Due to the higher toughness of the matrix, they offer a higher impact resistance. Manufacturing cycle times, which include melting the matrix, shaping and consolidation by cooling are significantly shorter than for their thermoset counterparts, which require a time consuming curing step. In addition, TPCs can be welded and recycled.

In structural composite applications, textiles are usually used as reinforcement due to the higher fibre volume fractions achievable and due to the possibility to tailor the load bearing capacity through the fibre lay-up. Traditionally, textile fibre-reinforced TPCs are processed through melt by stacking alternating layers of fibre

textiles and polymer sheets in a hot-press. After heating the layers above the polymer melting point, the press is closed and the required product shape is obtained. In a subsequent cooling step the product solidification occurs, followed by de-moulding. The main disadvantage of TPCs is the need for high processing temperatures and pressures, caused by the high melt viscosity of the matrix. In addition, an appropriate impregnation of the fibre at a microlevel is difficult often leading to products characterized by a high void content. A potential solution to improve the fibre impregnation is to bring the matrix and the fibres *"in more intimate"* contact before the final moulding step, or in other words, to reduce the required flow length of the polymer matrix. Various concepts of these intermediates have been developed such as co-mingled textiles that consist of both reinforcing and polymer fibres, textiles made of powder coated fibres and partially or fully consolidated panels (semi-pregs and pre-pregs ), see Figure 2.

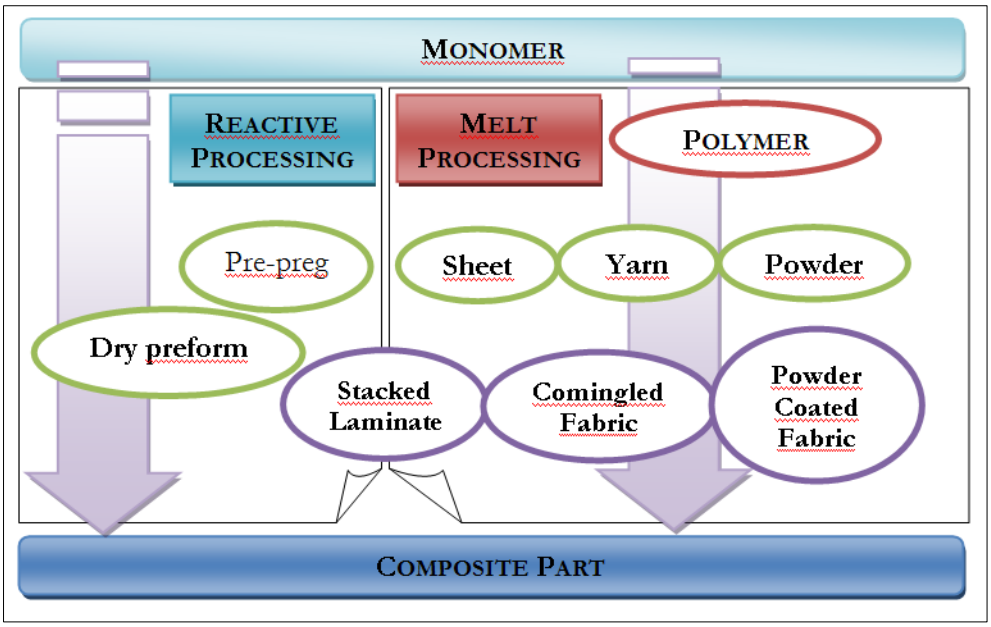


Figure 2 - Processing steps for manufacturing thermoplastic composite parts through melt- and reactive processing

Besides the additional costs of these intermediate products, further disadvantages are encountered such as the de-bulking of commingled textiles and the occurring fibre waviness, the adherence of the powder coatings and the occurrence of electrostatic discharges during processing of powder coated textiles. Semi- and pre-

pregs have poor drapability and often contain some solvent residue when they are made by solution impregnation.

## 1.3 Reactive processing of an epoxy-based thermoplastic system

An alternative solution to melt processing is represented by the reactive processing of TPCs: after impregnation, the polymerization of the thermoplastic matrix is conducted in situ. Polymerization can be initiated by heat or UV radiation and might require the addition of a catalyst, which can be added to the precursor before impregnating. Due to their low molecular weight, precursors have extremely low melt viscosity and proper fibre impregnation is consequently achieved without the need for high processing pressures. Moreover, through reactive processing, textile fibre reinforced TPCs can be even manufactured through low pressure infusion processes.

Additional advantages of this type of processing are:

- larger, thicker and more integrated products can be produced compared to what can be currently achievable through melt processing.
- a thermoplastic composite with a chemical fibre-to-matrix bond can be obtained, due to the fact that polymerization takes place when precursors are already in contact with fibres.
- in addition to the textile reinforcement, nano-particles can be added to the unreacted monomer in order to obtain a fibre-reinforced polymer nano-composite.

Van Rijswijk et al.[4] have published in 2006 an overview on thermoplastic material systems that can be reactively processed, making a distinction between engineering and high-performance plastics. Various reactive processes are discussed to manufacture fiber-reinforced thermoplastic products and the differences between reactive processing of thermoplastic and thermosetting resins were highlighted.

A summarized representation of melt viscosities and processing temperatures of various matrix materials for both reactive and melt processing is reported in Figure 3. Engineering plastics are neighbor of epoxy thermosetting resin in term of reactive processing temperatures and viscosities. Starting from this consideration, the idea of produce an epoxy-based reactive system which exhibit a thermoplastic behavior is not far away.

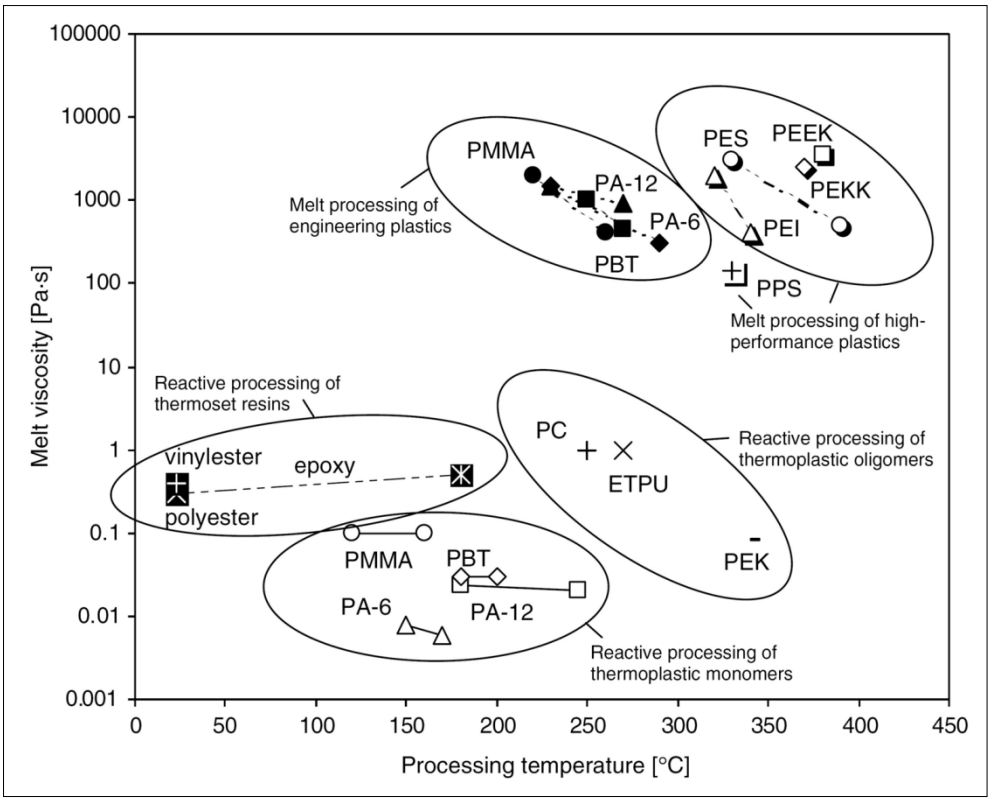


Figure 3 - Melt viscosities and processing temperatures of various matrix materials for both reactive and melt processing.[4]

## 1.4 Research outline

This work was organized as follow. After a brief introduction on thermoplastics and reactive processing for composite materials (chapter 1), two frames were devised. In the first one (chapters 2 and 3), were organized all works that concern the thermoplastic epoxy-based system development which has been carried out during this research work. In the second one, (chapters 4 and 5) were grouped some

potential applications of this system in the fields of nanocomposites and fibre-reinforced composites.

In the chapter 2 the state of the art on thermoplastic composites by reactive processing is presented and discussed. The intention was to bring into focus materials and processes, for which was developed a capable, integrated and optimized reactive processing. In the first part is detailed a survey on thermoplastic polymers, which are already adapted to be reactively processed. In the second part an overview on epoxy resin world was done. The basic chemistry of epoxy group and its application in reactive mixtures for thermosetting products are described. Some thermoplastic epoxy-based products, created for melt processing or as additives for other complex formulations (such as toughness modifiers for thermosetting polymers) are also reported. By merging the available know-how for epoxy-based thermoset matrices and the experiences developed for reactive thermoplastic systems, material designing guidelines were developed.

In the chapter 3, according with guidelines outlined in the previous chapter, the down selection process of material precursors was carried out. The early paragraph was focused on the formulation of the reactive mixture. Following, every aspects of formulation has been analyzed and an optimization procedure was carried out. Results of works reported in this chapter are the formulation and the polymerization procedure of a reactive epoxy-based mixture, which can be used as thermoplastic polymer matrix in long fibre reinforced composites.

In the chapter 4 polymer nanocomposites are introduced, in particular epoxy/carbon nanotubes composites. Various approaches to improve the dispersion, orientation, and adhesion of CNTs are reviewed. The core of this part is represented by nanocomposites manufacturing made by thermoplastic epoxy-based reactive system formerly developed. The resulting nanocomposite properties are described, by focusing on electrical and mechanical features

In chapter 5, the manufacturing of fibre reinforced polymer matrix composites was focused by describing processes already used for components using reactive

processing of non-epoxy thermoplastic or thermoset epoxy resins. Then, a detailed description of the process of a fibre reinforced item by reactive processing, employing the developed EPO formulation has been carried out. Results of the work reported in this chapter are the proof of feasibility and effectiveness of the reactive processing of EPO product and the reshaping after polymerization of the reinforced product.

## 1.5 References


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*PART A*

*THERMOPLASTIC EPOXY-BASED SYSTEM*

# 2.

# REACTIVE THERMOPLASTIC MATERIAL SYSTEMS

## 2.1 Summary

In this chapter the state of the art regarding thermoplastic composites by reactive processing is presented and discussed. The main target of this chapter it will be to focus reader's attention on materials and processes, for which a capable, integrated and optimized reactive processing was developed by this research work.

In the first part, a literature survey about thermoplastic polymers, already adapted to be reactively processed, is reported in details. Main requirements are analysed and discussed along with a description of the typical chemical reaction schemes. The reported material systems are categorized in engineering and high-performance plastics, and grouped on their characteristic chemical functional group. Finally, every group is singularly. Readers should gather the sufficient "know-how" regarding reactive processing on both materials and processes to identify suitably the working plan of the present research.

The second part is mainly oriented to a general overview of epoxy resins, today mainly used for thermosetting polymers. The basic chemistry of epoxy group and its application in reactive mixtures for thermosetting products are described. Thermoplastic epoxy-based products, created for melt processing or as additives for

other formulations, (i.e. as toughness modifiers for thermosetting polymers) are also introduced and describe for sake of completeness.

In the third part reactive processes are reported, with particular emphasis on their potential usage to manufacture components made of reinforced composite materials.

By merging the know-how already available for epoxy-based thermosetting matrices and the experiences achieved by the development of reactive thermoplastic material systems material designing guidelines were developed and proposed.

## 2.2 Thermoplastic polymers obtained by reactive processing

According to van Rijswijk et al.[1] , reactively processed thermoplastic materials are categorized suitably in two main classes, respectively, engineering and high-performance plastics. In this work, various reactive processes are considered for the manufacturing of fibre-reinforced thermoplastic products and most important differences between reactive processing of thermoplastic and thermoset resins are highlighted.

For reactive processing of thermoplastic composites, the in situ polymerization of the matrix essentially has to fulfil the following requirements:

- formation of polymer chains with high molecular weight and a mainly linear backbone structure;
- sufficiently high conversions, in order to obtain a narrow molecular weight distribution and eliminate the presence of original small reactive monomers in the final product.
- no generation of unwanted by-products during the whole process.

Suitable polymerization types are consequently narrowed down to addition polymerizations of mono and bi-functional species. For engineering and high-

performance plastics vinyl polymerization and ring-opening polymerization are most common.

### *2.2.1 Vinyl and Ring-opening polymerizations*

Vinyl polymers are polymers made from monomers having carbon–carbon double bonds. During polymerization the π bonds of double bonds are broken and the free electrons are used to join together monomer units to form a long chain of many thousands of carbon atoms containing only single bonds between atoms.

Ring-opening polymerization (ROP), instead, is based on a polymerization mechanism in which ring-shaped (cyclic) molecules are converted into linear monomers or oligomers and subsequently connected together into high molecular weight polymers without by-products generation. ROP can be used as a clean option for polymerization routes, in which there is generation of nasty by-products or are required large amounts of hazardous solvents are required. PEEK and PPS fabrication, for instance, makes use of high-boiling solvents such as diphenyl sulfone and dichlorobenzene[2, 3] ,while during production of polycarbonates toxic phosgene gas is used for interfacial phosgenation polymerization[4]. In addition, molecular weights obtained through ROP are generally higher than same polymer obtained through polycondensation reactions. This later mechanism occurs due to tow main reasons. Firstly, during the polycondensation process, the molecular weight needs to be controlled and, at the same time, it needs to be lowered in order to keep the melt viscosity within the processing window. Secondly, polymer chains are broken, in the subsequent purification step, during which unreacted monomer and catalyst residues are separated by physical (heat, high shear forces) and chemical (solvents) processes.

### *2.2.2 Reactive processing of engineering plastics*

In the following, suitable thermoplastic material systems for obtain engineering plastics by reactive processing are reported.

**Polyurethanes** (PU) are among the most widely applied materials especially developed for reactive processing[5]. Main precursors are di-isocyanates, which can react with di-alcohols via free radical vinyl polymerization very quickly (a few seconds, also) when processed near 60–80 °C, as is shown in Figure 4a. If diamines are used instead of di-alcohols to polymerize products are called polyureas, see Figure 4b. Most polyurethanes exhibit a thermosetting behaviour, although thermoplastic polyurethanes are made or commonly sold as fully reacted granules or powder for melt processing. Dubé et al.[6], however, demonstrated the feasibility of reactive injection pultrusion (RIP) of TPU composites based on the above mentioned chemistry. They verified that the high reactivity of the resin requires a fast responding process control system, since any deviation from ideal conditions (stoichiometry, temperature, pressure) can easily lead to a significant reduction in the final polymer properties.

In the last decade reactive processing of TPU based on a different type of chemistry was developed by Dow Chemicals (USA) and is now used by the Fulcrum Composites Company for the manufacturing of continuous fibre reinforced TPU profiles by pultrusion[7,8]. While most polyurethanes are reactively processed from their monomers, Fulcrum TPU is based on high molecular weight linear polymers, which can be processed using a depolymerization–repolymerization (DPRP) mechanism. Upon heating, depolymerisation is activated and a decrease of molecular weight takes place, resulting in a significant viscosity reduction. Subsequent cooling induces repolymerization and molecular weight rises again up to its starting value. A minimum viscosity of a few Pa s is obtained at a processing temperature of 270°C. Although further heating reduces the viscosity into the mPa·s range, the material loses its ability to repolymerize, and recyclability of the Fulcrum resin can be achieved through re-grinding and injection moulding. The injection-moulded material does no exhibit a significantly loss of mechanical properties.

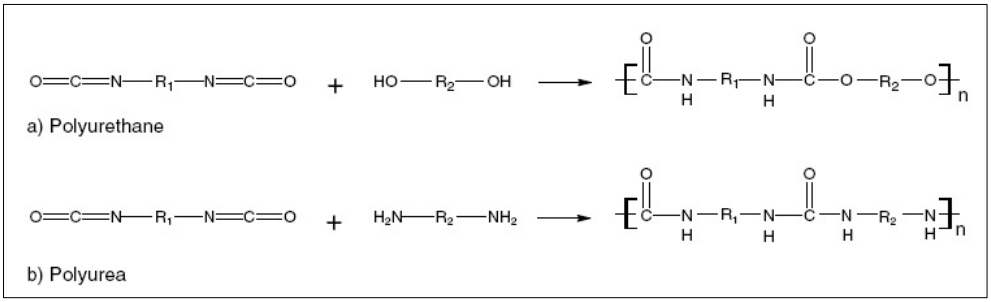


Figure 4 - Free radical vinyl polymerization of polyurethanes and polyureas

**Polymethylmethacrylate** (PMMA) can be obtained by free radical vinyl polymerization of the methylmethacrylate monomer (MMA). Polymerization is usually conducted using peroxide initiators. The main key parameter for this process is the temperature at which polymerization takes place: the high reaction heat (400-450 J/g) has to be quickly dissipated otherwise the monomer will soon start to boil, resulting in voids in the final product. During polymerization the density, also, increases from 0.9 g/cm$^3$ (monomer) to 1.2 g/cm$^3$ (polymer). In order to reduce shrinkage, and monomer over-temperature usually a pre-polymer (solution of PMMA in its monomer) is used. The melt viscosity of the pre-polymer is higher than that of the monomer (0.10 Pa·s at 50 °C), but is still low enough to cast (Plexiglas or Lucite) windows, which is the main application of PMMA due to its transparent nature. As far as composite processing is concerned, a monomer impregnation method of natural fibers and a reactive injection pultrusion process are mentioned in literature[9, 10]. In order to increase the reaction rate, which is necessary in a continuous process, the reaction temperature of the pre-polymer had to be increased to 160°C, which is well above the glass transition temperature of the amorphous polymer.

**Polyamides** are made by anionic polymerization of lactams, which is the oldest and up to now the most developed way for reactive processing of thermoplastics through ROP. In the early 1940s, ROP of caprolactam into PA-6 was discovered and has been commercially exploited by BASF, Bayern, DSM and Monsanto, for instance. Anionic polymerization of laurolactam into PA-12 has recently obtained

interest due to the work conducted at EMS Chemie A.G. and the Ecole Polytechnique Fédérale de Lausanne, both in Switzerland.

ε-caprolactam (Tm = 69 °C) into high molecular weight **polyamide-6** (PA-6) by catalyzed anionic ROP reaction (see Figure 5), performed at 130–170 °C [11]. Final conversions of up to 99.3% can be achieved in 3–60 min, by varying type and amount of activator and catalyst added. Typical activators used are N-acyllactams, whereas metal caprolactamates are commonly used as initiator[12]. Commonly the system is bi-component, two material batches are prepared: a monomer–activator batch and a monomer–initiator batch, which after mixing start to polymerize. Due to the anionic character, the reaction is easily terminated by proton donating species, such as for instance moisture. Hence, storage and processing have to be carried out in an absolutely moisture free environment. Since processing takes place below the polymer melting and crystallization point, polymerization and crystallization take place simultaneously, resulting in solid highly crystalline PA-6[13]. The reaction is exothermic ($\Delta H_{polymerization}$= -166 J/g, $\Delta H_{crystallization}$ = -144 J/g), which leads to a significant temperature increase during polymerization[14]. The complex kinetics of the anionic polymerization of caprolactam have been studied extensively, mainly focusing on the autocatalytic effect of the exothermic temperature rise[14, 15]. Numerous reactive processes have already been developed for unreinforced and reinforced PA-6 such as (rotational) casting , reaction injection molding (RIM), reinforced reaction injection molding (RRIM), structural reaction injection molding (SRIM)[16] and reactive injection pultrusion (RIP)[17]. Technology developed by DSM allows PA-6 to be fully depolymerized in a cost-effective way into caprolactam of virgin quality . In order to reduce mold shrinkage and to increase the toughness, a rubber-modified block-copolymer called Nyrim was developed by DSM and is currently traded under the name of AP Nylon by Brüggemann Chemical, Germany [65–69]. Due to the pre-polymer activator of AP Nylo, the viscosity is slightly higher (g = 60–90 mPa·s)[18] than of the unmodified resin (g = 10 mPa·s)[19]. In addition to these rubber block copolymers also varieties with branches and cross-links have been investigated[20]. A vacuum infusion process for manufacturing of

polyamide-6 composite wind turbine blades is currently being developed at The Delft University of Technology[19, 21].

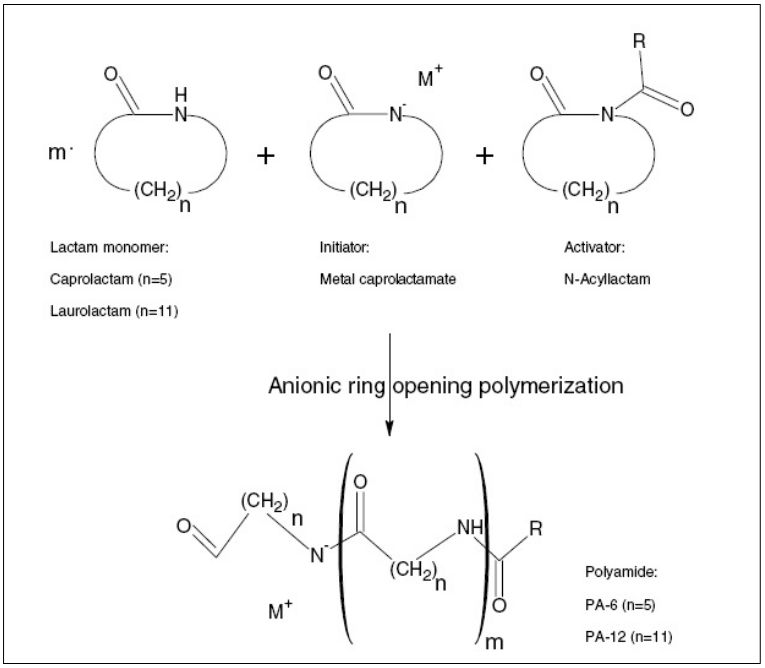


Figure 5 - Anionic ring-opening polymerization of polyamides

**Polyamide-12** is anionically polymerized from ξ-laurolactam (Tm = 154 °C) using similar activators and initiators as discussed for PA-6 [22], see Figure 5**Errore. L'origine riferimento non è stata trovata.**. Differently to PA-6 reactive process, polymerization has to be conducted above the final polymer melting point (175 °C), in order to increase the polymerization rate and to avoid early crystallization. Consequently, when process was performed at 180–240 °C, before demolding an additional cooling step is required. The molten monomer has an initial viscosity of 23 mPa·s and has to be kept in nitrogen protective environment to prevent initiator deactivation. The reaction exotherm heat is about 53 J/g] and total mold shrinkage is 8.3–9.6%. Reactive PA-12 is currently marketed by EMS Chemie A.G., Switzerland, who also developed a one part activator–initiator solution called Grilonit that can be stored indefinitely in inert atmosphere. Pultrusion[23] and SRIM like processes [24, 25] for PA-12 composites are currently being developed at the Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, the National University

of Ireland, Ireland and the Institut für Verbundwerkstoffe, Germany. Caprolactam and laurolactam can be anionically copolymerized to tailor polymer properties. Material properties such as the strength and stiffness, glass transition and the melting point are in direct relation with the monomer ratios.

Synthesis of macrocyclic **polyesters** and the ring-opening metathesis polymerization (ROMP) thereof was initially developed by D.J. Brunelle and his research group at the General Electrics Corporation, USA, in the late 1980s and early 1990s. Initially aiming at polycarbonates, see next paragraph, reactive processing of both polyetherteraphthalate (PET) and polybutyleneteraphthalate (PBT) was developed. This latter is currently being marketed specifically for the production of composites under the name Cyclics by the Cyclics Corporation, USA.

Macrocyclic oligomers can be obtained through cyclodepolymerization (CDP) of **linear PET** and subsequently repolymerized through ROMP into high MW PET [26]. Up to 100% conversion at 250–325 °C are obtained in several hours without a catalyst, whereas addition of a catalyst reduces the reaction time to 3–15 min at 225 °C. The initial melt viscosity of the cyclic precursors is 30 mPa·s[27].

Depolymerization of **linear PBT** produces a macrocyclic oligomer mixture, which can be repolymerized directly into solid high molecular weight (Mw = 445,000) semi-crystalline PBT at 180– 200 °C by using a titanium-based initiator[28]. The oligomer mixture has a melt viscosity ranging between 150 mPa·s at 150 °C, and 30 mPa·s at 190 °C. When processed at 190 °C in protective atmosphere, the viscosity reaches 1000 mPa·s after approximately 5 min and final conversions of 95–99% are obtained within 30 min. Polymerization is not exothermic, conversely a latter crystallization take place by releasing approximately 67 J/g . Final polymer properties strongly depend upon the polymerization temperature. When isothermally polymerized below its melting point ($T_m$ = 220–267 °C), the PBT obtained is highly crystalline and tends to become brittle (i.e. elongation at break = 1.8%), due to a phenomena called cold-crystallization. A subsequent melting and cooling cycle brings back the more ductile behavior. Properties of initially reactively processed PBT are basically unaltered by mechanical–thermal recycling (re-grinding

followed by injection molding)[29]. In addition, PBT can be recycled chemically by depolymerization into the cyclic oligomers or all the way into its monomers dimethylterephthalate and butanediol. RTM-like processes for the manufacturing fiber reinforced PBT are developed at Delaware University (USA) and KU Leuven (Belgium)[30], whereas the National University of Ireland is developing Resin Film Infusion technology, making use of a one-component monomer–catalyst system. Through ring-opening polymerization, PBT copolymers with PET can be easily obtained[28].

Macrocyclic Bisphenol-A ($T_m$ = 200–210 °C) can be polymerized into **polycarbonate** through ROMP conducted at 240–280 °C using anionic activators [108]. When polymerized at 250 °C in protective atmosphere, the initial viscosity of the macrocyclic melt is 1 Pa·s and in 2–5 min high molecular weight PC is reached (Mw = 300,000) with high conversions (over 99%). The reaction is entropy driven, which means that no exothermic heat is generated during polymerization. ROMP of macrocyclics consisting of Bisphenol-A and hydroquinone at 300 °C results in a solvent resistant PC, which can be obtained in either amorphous or semi-crystalline form[31]. Other versions reported in literature are cross-linked and copolymerized PCs[31] . Salem et al. successfully produced glass fiber reinforced PC composites through reactive processing, although an additional consolidation step in a hot-press was necessary to reduce the void content.

### *2.2.3 Reactive processing of high-performance plastics*

After the advances of reactive processing of engineering plastics such as PU, PMMA and PA-6, some trials were made to develop similar technology for processing of high-performance plastics, mainly focusing on ROP of polyarylethers. Initial results, however, made evidence of some complications, which were directly related to the inherent properties of high-performance plastics: an extreme stiff polymer backbone combined with outstanding chemical resistance and thermal properties. Whereas the relatively flexible engineering plastics are easily converted into cyclic precursors of only a single or a few monomer units, a much larger number of monomer units is required to form so-called macrocyclic precursors of

the more rigid high-performance plastics. The higher molecular weight of the cyclic precursors brings up the following problems:

- Synthesis of the cyclic precursors has to be carried out in high-dilution or pseudo-high-dilution conditions, in order to obtain the ring closure reaction. If linear precursors concentration during synthesis is too high, it is more probable that a chain will react with a neighboring chain rather than having its two ends react together to form a cycle. Synthesis therefore requires a lot of solvent and leads to relatively low efficiency.

- The macrocyclic precursors obtained are often an oligomer blend. Different oligomers might differ in properties such as melting points, solubility in the other oligomers within the same mixture or even in being amorphous of crystalline. These differences complicate synthesis and further processing.

- To obtain high conversions, polymerization has to be conducted at high temperatures. Firstly because the processing temperature has to exceed the melting point of all oligomers, secondly for the reason that the viscosity of the growing polymer chains has to be kept low enough to induce sufficient chain mobility. Unfortunately, at temperatures ranging from 300 to 400 °C side reactions like cross-linking are unavoidable, which strongly reduce the polymer performance.

Recent advances in cyclics technology are:

- the use of monomer units containing meta and ortho rather than para backbone substructures in order to create macrocyclics with a lower molecular weight. This choice bring to a slight reduction of thermal stability of their equivalent polymer.

- Selection of specific oligomers with a low melting point, which prevent crystallization, to reduce the required polymerization temperature.

An overview of reactive processing equivalents of common high-performance plastics is reported below..

For **polyetheretherketone (PEEK)**, in literature are mentioned synthesis of 45–60–90 membered macrocyclics from 4,4-difluorobenzophenone and hydroquinone in pseudo-high-dilution conditions at a yield of 60%, which polymerized at 350 °C in 5 min using caesium fluoride as initiator[32]. Another source reports synthesis of cyclic 2-mers, 3-mers and 4-mers, but fails to discuss ring-opening polymerization[33].

Jiang et al.[34] manufactured macrocyclic oligomers for **polyetherketones (PEK)** with a yield of 54%. These cyclics ($T_g$=127 °C) formed a clear melt at 280°C and could subsequently be polymerized for 1 h at the same temperature up till a conversion of 93.5%. The obtained linear polymer is slightly branched and has a $T_g$ of 216 °C, which is slightly lower than commercially produced PEK (Tg = 228 °C), due to the presence of oligomers that failed to polymerize. Ring-opening polymerization at 390 °C for 30 min of a cyclic PEK dimer into an amorphous polymer (Tg = 162 °C) was reported by the same authors. The potential of reactive processing of high performance thermoplastics is clearly demonstrated by the work performed at McGill University, Canada [35]. It was shown that macrocyclic PEK containing a 1,2-dibenzoylbenzene moiety, see Fig. 9, has a stable melt viscosity (80 mPa s at 330 °C) and it could be polymerized at 340 °C in 30 min after addition of a nucleophilic initiator. Baxter et al.[36] managed to polymerize cyclic PEK in 30 min at 300 °C using a Caesium fluoride initiator into a semi-crystalline polymer (Tg = 168 °C, Tm = 302 °C). In addition, they showed that instead of using macrocyclics specifically synthesized for ring-opening polymerization, one could also use the cyclic oligomer byproduct that is generated during production of commercial PEK-390 and polymerize these in 25 min at 385 °C.

**Polyethersulfone (PES)** was also obtained by ROP of cyclic precursors, conducted at 300 °C for 2 h.[37].

Melt polymerization of cyclic **Polyphenylenesulfide (PPS)** pentamer and hexamer at 300 °C under Nitrogen environment is discussed by Miyatake et al. [38]. The

resulting high molecular weight polymer is highly crystalline and has a melting point of 277 °C, which is comparable to that of commercial grades PPS (Tm = 285 °C). An alternative method for preparing the same cyclic PPS precursor is discussed by Wang et al.[39].

According to Hubbard er al.[40], a **polyethylenenaphthalate (PEN)** macrocyclic oligomer mixture with a melting point of 250–285°C was prepared in a 57% yield. In 25 min ROP was conducted in the presence of a peroxide initiator at 295–300°C. The final polymer ($T_m$= 261°C) affected by impurities presence in the cyclic oligomer mixture and initiator residue.

**Polybutylenenaphthalete (PBN)** macrcocylic precursors containing various size oligomers ($T_m$ = 150–220 °C) were prepared at a 75% yield. ROP was subsequently conducted in the presence of a tin oxide catalyst at 275 °C and was completed in 15 min. The linear low molecular weight impurities in the cyclic oligomer mixture strongly affected the final polymer properties[40].

To summarize this section, the processing temperatures for common thermoplastic matrices discussed above for both melt- and reactive processing are reported in Table 1. For comparison Figure 3 in chapter 1 shows the melt viscosities and processing temperatures of different mono and oligomeric thermoplastic precursors. The same data are also given for common thermoset resins and thermoplastic polymers generally employed in melt processing.

The following main focuses can be suitably highlighted:

- whereas the reduction in processing temperatures for engineering plastics is significant, the difference for high-performance plastics is relatively small. The reason for this is the high melting point of the oligomeric precursors for high-performance plastics, which are almost as high as their high molecular weight linear equivalents.

- polymers which can be obtained by ROP reactions needs special precursors, especially designed e produced. This characteristic is not clearly a cost

effective solution and an industrial scale-up can be reasonable only for massive and highly standardized manufacturing, like automotive non structural components, by way of example.

- polymers, based on epoxy chemistry, are not fully developed to obtain thermoplastic matrices, by bulk reactive process. Although epoxy-based resins are the main massive thermosetting matrices for standard and advanced micro and nano composites. Epoxy groups, also, show a wide range of reactivity: their chemical versatility can be well used to formulate a reactive mixture, which can comprise their good processing property and their potential to achieve a thermoplastic matrix for composite materials.

Table 1 - Comparison of processing temperatures for melt- and reactive processing for some common thermoplastic matrix materials[1]

| **Thermoplastic matrices - Processing temperature (°C)** | | | |
|---|---|---|---|
| | Melt processing | Reactive processing | Reduction |
| PA-6 | 230–290 | 140–160 | 70–150 |
| PA-12 | 230–270 | 180–245 | 0–90 |
| PBT | 250–270 | 180–200 | 50–90 |
| PMMA | 220–260 | 120–160 | 60–140 |
| PC | 265–360 | 250 | 15–110 |
| PET | 265–325 | 250–325 | 0–15 |
| PES | 330–390 | 300 | 30–90 |
| PPS | 330 | 300 | 30 |
| PEEK | 380–390 | 350 | 30–40 |

## 2.3 Epoxy resins

The term epoxy, epoxy resin, or epoxide refers to a wide group of reactive compounds that are characterized by the presence of an oxirane or epoxy ring. This is represented by a three-member ring containing an oxygen atom that is bonded

with two carbon atoms already united in some other way. An epoxy resin can be any molecule containing more than one of these epoxy groups. The number of epoxy groups per molecule is the functionality of the resin. The groups can be situated internally, terminally, or on cyclic structures. Epoxy groups are capable of reacting with suitable curing agents or catalytically (homopolymerized) to form higher-molecular-weight polymers. In general, once cured, the epoxy polymers have a densely cross-linked, thermosetting structure with high cohesive strength and adhesion properties. However, the term epoxy can also be used to indicate an epoxy resin in the thermoplastic or uncured state. A general formula for an epoxy resin can be represented by a linear polyether with terminal epoxy groups and secondary hydroxyl groups occurring at regular intervals along the length of the chain. The epoxy resin structure and properties influenced by the various chemical groups are illustrated in Figure 6. Several important considerations can be made regarding the structure of the epoxy molecule:

- the epoxy groups at both terminals of the molecule and the hydroxyl groups at the midpoint of the molecule are highly reactive.

- the outstanding adhesion of epoxy resins is largely due to the secondary hydroxyl groups located along the molecular chain; the epoxy groups are generally consumed during cure.

- the large part of the epoxy resin backbone contains aromatic rings, which provide a high degree of heat and chemical resistance.

- the aliphatic sequences between ether linkages confer chemical resistance and flexibility.

- the epoxy molecule can be of different molecular weight and chemistry. Resins can be low-viscosity liquids (LERs, liquid epoxy resins) or hard solids at room temperature or above (SERs, solid epoxy resins).

- a large variety of polymeric structures can be obtained by varying the polymerization reaction and the curing agents involved. This can lead to

versatile resins that can cure slowly or very quickly at room or at elevated temperatures. No small molecules such as water are released during the curing process. Thus, epoxies exhibit low shrinkage, and they can be cured under very low pressure. This provides an adhesive joint with a very low degree of internal stress when cured.

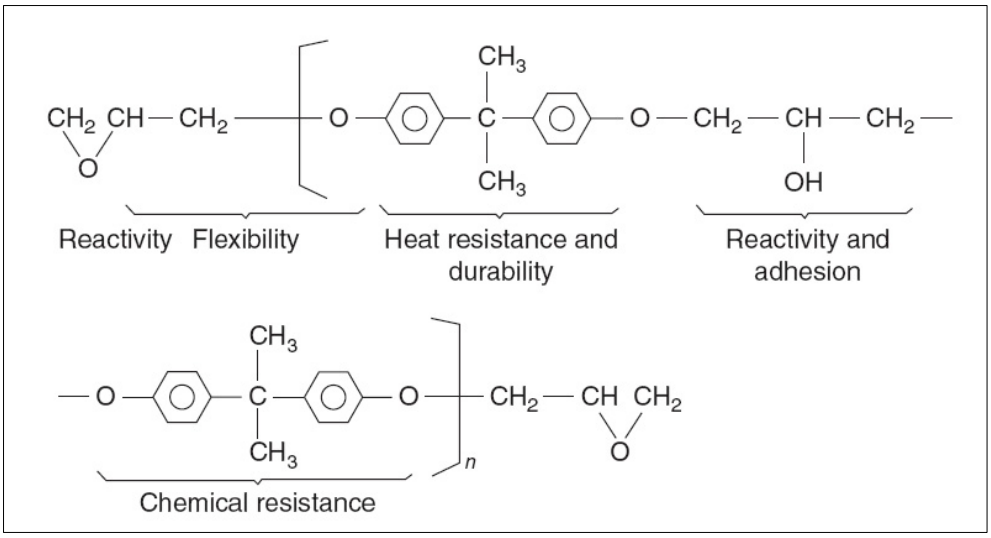


Figure 6 - Typically epoxy resin structure[41]

Epoxy resins, already on the market, are not necessarily completely linear or terminated with epoxy groups. Some degree of branching occurs, with the end groups being either epoxy or hydroxyl. The amount and degree of branching vary from resin to resin and from supplier to supplier. Epoxy resins are not completely difunctional. Tri-, tetra-, and polyfunctionality are probable. Various end groups can be introduced as a consequence of the manufacturing process. The ratio of the main ingredients used in the synthesis of epoxy resins (epichlorohydrin: bisphenol A) determines the extent of the reaction and the molecular weight (or value of n repeating units in the molecular chain). The addition of bisphenol A to the reaction mix will advance the molecular weight of the resin and the value of n. As n increases, the viscosity or melting point of the resin also increases. Also as the value of n increases, the number of hydroxyl groups increases while the number of epoxy groups remains constant. An important term that is used in formulating epoxy reactive compositions is epoxy equivalent weight (EEW). This is defined as the

weight of resin in grams that contains one equivalent of epoxy. As the resin's molecular weight increases, the EEW will also increase. EEW is used to evaluate quickly the amount of co-reactive curing agents.

### *2.3.1 Curing of Epoxy Resins*

Almost all epoxy resins are converted into solid, infusible and insoluble three-dimensional thermoset networks by curing with cross-linkers for obtain final products. Some exceptions are represented by very high MW phenoxy resins and epoxy-based thermoplastic resins, described in the next paragraphs. These products have not gathered a large market so far.

Optimum performance properties are achieved by cross-linking the right epoxy resins with the proper cross-linkers, often called hardeners or curing agents. The selection of the suitable curing agent is determined by the requirements of the application process techniques, pot life, cure conditions, and ultimate physical properties. The choice of curing agent, also, affect viscosity and reactivity of the formulation, and determines both the types of chemical bonds formed and the degree of cross-linking that will occur. These features, in turn, affect the chemical resistance, electrical properties, mechanical properties, and heat resistance of the cured polymer.

Epoxy resins contain two chemically reactive functional groups: epoxy and hydroxy. Low MW epoxy resins such as LERs are considered difunctional epoxy monomers or prepolymers and are mostly cured via the epoxy group. However, as the MW of SERs increases, the epoxy content decreases, whereas the hydroxyl content increases. High molecular weight SERs can cross-link via reactions with both the epoxy and hydroxyl functionalities, depending on the choice of curing agents and curing conditions.

Reaction of the epoxy groups implicates the opening of oxirane ring and the creation of longer, linear C-O bonds. These two mechanisms accounts for the low shrinkage and good dimensional stability of cured epoxies. The use of some curing

agents can lead to a polycondensation reaction, which is accompanied by the generation of volatile by-products, such as water or alcohol, requiring heat for proper cure and volatiles removal. It is the unique ability of the strained epoxy ring to react with a wide variety of reactants under many diverse conditions that gives epoxies their versatility[42].

Detailed discussions on the probable electronic configurations, molecular orbitals, bond angles, and reactivity of the epoxy ring are available in the literature. Compared to non-cyclic and other cyclic ethers, the epoxy ring is extremely reactive. It has been postulated that the highly strained bond angles, along with the polarization of the C-C and C-O bonds, account for the high reactivity of the epoxide. The electron-deficient carbon can be subjected to nucleophilic reactions, whereas the electron-rich oxygen can react with electrophiles. It is customary in the epoxy industry to refer to these reactions in terms of anionic and cationic mechanisms. The terminology was attributed to the fact that an anionic intermediate or transition state is involved in a nucleophilic attack of the epoxy while a cationic intermediate or transition state is formed by an electrophilic curing agent[42].

Curing agents can be classified in catalytic or co-reactive. A catalytic curing agent plays a role as initiator for epoxy resin homopolymerization or as accelerator for other curing agents, while the co-reactive curing agent works as a reactive co-monomer in the polymerization process (see Figure 7).

The most of the epoxy reactive mixtures are formulated basically on reaction sets based on nucleophilic mechanisms. The main groups of co-reactive curing agents are those with active hydrogen atoms: primary and secondary amines, phenols, thiols, and carboxylic acids (and their anhydride derivatives). Lewis acids, like boron trihalides, and Lewis bases, like tertiary amines, are used as initiators.

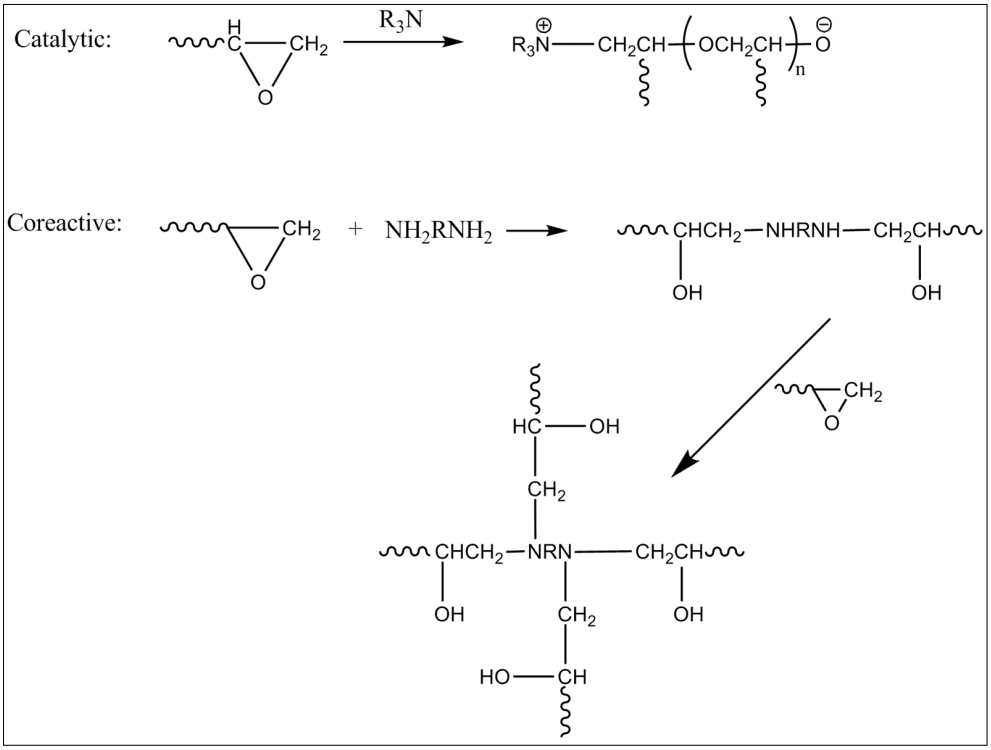


Figure 7 - An example of catalytic and coreactive basic reaction schemes

The functional groups surrounding the epoxide resin also affect the curing process. Steric factors can influence ease of cure. Electron-withdrawing groups adjacent to the epoxide ring often enhance the reactivity of the epoxy resin to nucleophilic reagents, while retarding its reactivity toward electrophilic reagents. In general, aromatic and brominated aromatic epoxy resins react quite readily with nucleophilic reagents, whereas aliphatic and cycloaliphatic epoxies react slowly toward nucleophiles[42].

Clearly epoxy structure significantly influences the cure response as a function of pH. Cycloaliphatic epoxies are fast-reacting under low pH conditions. Aromatic glycidyl ethers are faster under high pH conditions. These results generally agree with "practical" cures: aromatic epoxies are easily cured with amines and amidoamines. Cycloaliphatics are cured with acids and superacids. The behavior of the aliphatic epoxies is more complex but on balance is similar to that of cycloaliphatics.

The most commonly used curing agents are amines, followed by carboxylic functional polyesters and anhydrides.

### *2.3.2 Phenoxy Resins*

Phenoxy resins are thermoplastic polymers derived from bisphenol A and epichlorohydrin. Their weight-average molecular weights (Mw) are higher (ie, >30,000) than those of conventional SERs (ie, 25,000 maximum). They lack terminal epoxides but have the same repeat unit as SERs and are classified as polyols or polyhydroxy ethers:

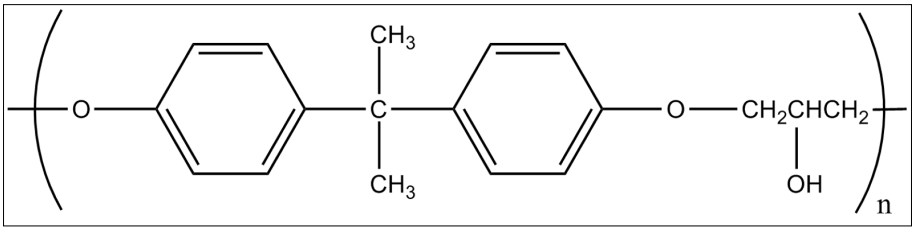


Figure 8 - Repeating unit in a phenoxy thermoplastic resin

Phenoxy resins were originally developed and produced by Union Carbide (trade names PKHH, PKHC, PKHJ) using the taffy process. The process involves reaction of high purity bisphenol A with epichlorohydrin in a 1:1 mole ratio. Alternatively, phenoxy resins can be produced by the fusion process which uses high purity LER and bisphenol A in a 1:1 mole ratio. High purity monomers and high conversions are both needed to produce high MW phenoxy resins. The effects of monomer purity on phenoxy resin production are significant: monofunctional components limit MW, and functionality >2 causes excess branching and increased polydispersity. Solution polymerization may be employed to achieve the MW and processability needed. This, however, adds to the high costs of manufacturing of phenoxy resins, limiting their commercial applications. The phenoxies are offered as solids, solutions, and waterborne dispersions. The majority of phenoxy resins are used as thermoplastics, but some are used as additives in thermoset formulations. Their high MW provide improved flexibility and abrasion resistance. Their primary uses are in automotive zinc-rich primers, metal can/drum coatings, magnet wire

enamels, and magnetic tape coatings. Smaller volumes of phenoxy resins are used as flexibility or rheology modifiers in composites and electrical laminate applications, and as composite honeycomb impregnating resins[42]. However, they can be crosslinked through their epoxy groups and, more conveniently, through the hydroxyl groups (through reaction with isocyanates or melamine formaldehyde resins) along the molecular chain. Phenoxy resins have considerable mechanical strength by themselves and are often used as unformulated thermoplastic hotmelt adhesives[41]. A new, emerging application is fiber sizing, which utilizes waterborne phenoxies. Literature references indicate their potential uses as compatiblizers for thermoplastic resins such as polyesters, nylons, and polycarbonates because of their high hydroxyl contents. Current producers of phenoxy resins include the Phenoxy Specialties division of InChem Corp., Resolution, Huntsman, Tohto Kasei, and DIC.

### *2.3.3 Epoxy-Based Thermoplastics*

Some of the new epoxy products developed in the past few years are the thermoplastic resins based on epoxy monomers. Polyhydroxy amino ether[43] (PHAE) was commercialized by Dow Chemical in 1999 and trade named BLOX∗ (see Figure 9). It is produced by the reaction of DGEBA with monoethanol amine using the reactive extrusion process. The high cohesive energy density of the resin gives it excellent gas-barrier properties against oxygen and carbon dioxide. It also possesses excellent adhesion to many substrates, optical clarity, excellent melt strength, and good mechanical properties. The product has been evaluated as a barrier resin for beer and beverage plastic bottles, as thermoplastic powder coatings, and as a toughener for starch-based foam. Another epoxy thermoplastic resin under development by Dow is the polyhydroxy ester ether (PHEE). It is a reaction product of DGEBA with difunctional acids. The ester linkage makes it suitable for biodegradable applications[44].

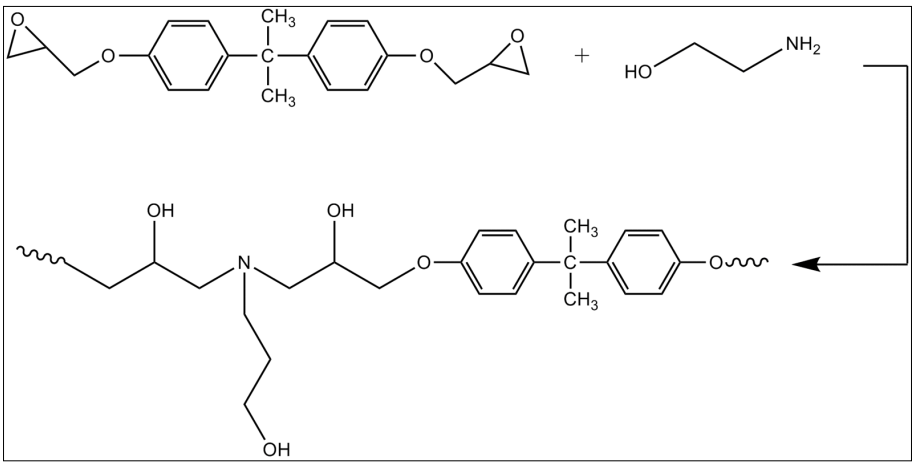


Figure 9 - Poly hydroxyl amino ether (PHAE) resins

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# 3.

# REACTIVE THERMOPLASTIC EPOXY-BASED SYSTEM

## 3.1 Summary

In this chapter, according with guidelines outlined in the previous chapter, the down selection process of material precursors was carried out.

The early paragraph was focused on the formulation of the reactive mixture, by pointing up the main features, which has to be combined to bring a formulation able to produce the final material by an effective reactive process.

In the next, every aspect of formulation has been analyzed: for every required mix component a selection procedure was carried out and every choice was run out by experimental testing. The polymerization process was analyzed and an optimization procedure was carried out.

Results of works reported in this chapter are the formulation and the polymerization procedure of a reactive epoxy-based mixture, which can be used as thermoplastic polymer matrix in reinforced composites. A material characterization was, also, carried out.

## 3.2 Formulation Development with Epoxy Resins

The most important step in using epoxy resins is to develop the appropriate epoxy formulation since most are used as precursors to obtain finally a three-dimensional cross-linked network[1]. Our target, instead, is to obtain a thermoplastic polymer, in which, during polymerization process, linear chain growth is preferred to highly

cross-linking rates. With the exception of the very high molecular weight phenoxy resins and the epoxy based thermoplastics for hot melt processing, epoxy resin is rarely used by itself. It is frequently formulated with modifiers such as fillers and used in composite structures with reinforcements fibres or coatings on metal substrates.

To design a successful epoxy formulation that will give optimum processability and performance, the following features must be carefully considered[2]:

- selection of the suitable combination of epoxy resin(s) and curing agent(s) chemical structures
- epoxy/curing agent stoichiometric ratio
- selection of catalyst/accelerator
- curing/post-curing processes and conditions
- formulation modifiers such as fillers, diluents, toughening agents, etc.
- interactions among the formulation ingredients and with the composite materials (fibres, metals, etc) on the system chemistry, adhesion, rheology, morphology and performance

The development of an epoxy formulation containing a high number of components can be very resource and time consuming. Techniques such as design of experiments (DOE) are useful tools to facilitate the formulation development process and to obtain optimum performance. The adopted approach is to maximize the know-how transfer from thermosetting epoxy-based formulation experiences and to narrow the precursors selection among precursors, which already used for other applications and can be considered cost effective solutions.

### *3.2.1 Relationship Between Polymerized Epoxy Resin Structure and Properties*

The concept originated with the rubber elasticity theory developed for the lightly cross-linked elastomers has been adopted with success for epoxy thermoset polymers. The cured epoxy system derives its properties mostly from a combination of cross-link density, monomer structure and the curing process. The structure existing in a cross-linked network, such as the position of the nodes in the network, as well as the distance between them are important characteristics to take into account for studying the formulation of an epoxy system. Molecular weight between cross-links (Mc) and cross-link density are terms developed to describe "distance" between cross-link nodes. Cross-link density increases with degree of cure up to its limit at full conversion of the (limiting) functional groups.

In order to obtain an epoxy-based thermoplastic polymer, these concepts has to be overturned. The main key aim it is not to obtain an high cross-linked network, using co-reactive agents as linkers between more epoxy terminated chains. A thermoplastic polymer can be obtained by block co-polymerization, in which epoxy terminated precursor and co-reactive agents are the co-monomers. By alternating these two blocks linear chain growth is obtained and high molecular weights are reached. Macromolecules obtained in this way form a physical network, their mobility can be increased growing up temperature, then can be melted.

During polymerization process collateral reactions can occur: small branching, caused by lateral grafting chain growth cannot be fully avoided, and can lead to a low cross-linking degree. Grafted chains are not fully unwanted: if polymer chain regularity is not strictly kept, crystallization will be prevented: an amorphous polymer is the best result for our applications. Cross-linking, also, has to be precluded, but a slight cross-linking can be helpful to obtain a small fraction of high weight molecules, which can improve mechanical and thermal properties of the final product.

How the epoxy resin structure and properties influenced by the various chemical groups are, also, illustrated in Figure 6. Then, several important statements can be made relative to the relationship structure/properties of the epoxy final product:

- the epoxy co-monomers has to be bi-functional, with the epoxy groups at both terminals of the molecule, other reactive groups, such as hydroxyl groups at the midpoint of the molecule, has to be avoided, because they are highly reactive, and can produce grafting e cross-linking.

- the final outstanding adhesion of epoxy resins is largely due to the secondary hydroxyl groups located along the molecular chain, which are generated by reaction and consumption of the epoxy groups during polymerization. These hydroxyl groups can also react during polymerization with other epoxy activated groups, then they can produce grafting and/or cross-linking, which must be controlled and minimized.

- the large part of the epoxy resin backbone contains aromatic rings, which provide heat and chemical resistance, mechanical rigidity, but, also, an high chain regularity. Then a consequent partial crystallization can occurs, which can be hindered by the presence of grafted chains o some cross-links.

- the presence of aliphatic sequences can confer flexibility, and balance the rigidity provided by aromatic ring to obtain a final product with good toughness properties .

## 3.3 Precursors Selection

Successful performance of epoxy-based systems depends on proper selection and formulation of components. The precursors that have the most significant influences, both for processability, both for the final properties, are the epoxy resins and the curing agents. As mentioned above, the precursor selection was narrowed, as possible, among which already used for other applications and can be considered cost effective solutions. Industrial research in the latest years produced the largest variety of precursors for polymer applications, then the material design has to be

focused not on the synthesis of new precursors, rather the formulation of reactive mixtures, which produce materials having programmed properties, using optimized and integrated manufacturing processes.

### *3.3.1 Selection of Epoxy Resins*

There are many choices of epoxy resins and curing agents, presenting a wide variety of structure and functionality. Figure 10 shows the general attributes of common types of epoxy resins.

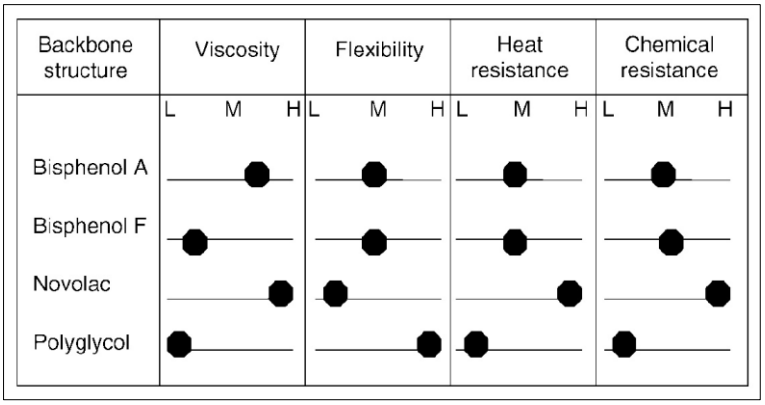


Figure 10 - Comparison of relative properties of common epoxy resins. L, low; M, medium; H, High[2]

Epoxy resins can be used separately or in combination, such that formulations can be designed to take advantage of the desirable characteristics of several components. Because combining resins from different families can result in certain trade-offs, a careful balance of components should be investigated to produce optimal performance for specific applications.

As explained above, among commercial epoxy resins the first choice to obtain a thermoplastic product is the bi-functional epoxy precursor, then novolacs are surely excluded because of their multiple functionality and high viscosity, which make difficult reactive processing of fibre reinforced composites. Then the right solution are, certainly, di-glycidyl ethers, in particular bisphenol A di-glycidyl ether (DGEBA). Bisphenol F di-glycidyl ether (DGEBF), in addition, offer a lower viscosity in the uncured state, against an higher price. DGEBA has viscosity levels

fully compatible with reactive processes of fibre reinforced composites, then DGEBF can be used as partial substitute in case of particular applications, without altering other key parameters.

Bi-functional DGEBA resins are offered commercially in a wide range of molecular weights. As the molecular weight increases, so does the chain length between the epoxy end groups. These oligomers are made by homopolymerization reactions and are classified using the number-average degree of polymerization, *n*, which approximates the repeating units and the hydroxyl functionality of the resin. Table 2 shows the effects of increasing EEW and MW of bisphenol A based epoxy resins on resin properties.

In epoxy formulation for obtain thermosetting polymers the cross-link density of a bi-functional resin cured by way of the epoxy group decreases as the resin molecular weight increases. High molecular weight resins are frequently cured via the secondary hydroxyl group, chemistry that results in a different set of structure–property relationships. Multifunctional epoxy resins are available with functionalities ranging from above 2 to about 5. When cured to the same degree using a given curing agent at stoichiometric ratios, they produce a higher cross-link density, higher glass transition temperature, better thermal and chemical resistances compared with bi-functional epoxy resins.

Conversely, to obtain epoxy-based thermoplastic polymers, the smallest cross-linking density has to be reached using bi-functional DGEBA with low molecular weight, that is, the smallest precursor, which has the number-average degree of polymerization minor then 0.1. That's because lower is the hydroxyl functionality of the resin, lower is the cross-link possibility through the reaction between hydroxyl functionality and an epoxy ring. The commercial product which can be used is the DER331 epoxy resin by Dow Chemicals (properties reported in Table 3), or an equivalent product.

High purity epoxy precursors are needed: the presence of multifunctional epoxy molecules can lead to unwanted branched polymers, which affects final processing

properties. High purity liquid bisphenol A di-glycidyl ether (DGEBA) epoxy resins, as well as the liquid bisphenol F di-glycidyl ether (DGEBF) epoxy resins, are also super-cooled liquids at room temperature.

Table 2 - DGEBA-based epoxy resins, precursors properties[2]

| Resin type | *n* [a] | EEW | Mettler softening point, °C | Molecular weight (Mw)[b] | Viscosity at 25°C, mPa·s (= cP) |
|---|---|---|---|---|---|
| Low viscosity LER | *<0.1* | 172–176 | | ~350 | 4,000–6,000 |
| Medium viscosity LER | ~0.1 | 176–185 | | ~370 | 7,000–10,000 |
| Standard grade LER | ~0.2 | 185–195 | | ~380 | 11,000–16,000 |
| Type 1 SER | ~2 | 450–560 | 70–85 | ~1,500 | 160 – 250[c] |
| Type 4 SER | ~5 | 800–950 | 95–110 | ~3,000 | 450 – 600[c] |
| Type 7 SER | ~15 | 1,600–2,500 | 120–140 | ~10,000 | 1,500–3,000[c] |
| Type 9 SER | ~25 | 2,500–4,000 | 145–160 | ~15,000 | 3,500–10,000 |
| Type 10 SER | ~35 | 4,000–6,000 | 150–180 | ~20,000 | 10,000–40,000[c] |
| Phenoxy resin | ~100 | >20,000 | >200 | >40,000 | |

[a] n value is the number-average degree of polymerization which approximates the repeating units and the hydroxyl functionality of the resin.
[b] Molecular weight is weight average (Mw) measured by gel-permeation Chromatography (GPC) using polystyrene standard.
[c] Viscosity of SERs is determined by kinematic method using 40% solids in di-ethylene glycol mono-butyl ether solution

These resins are supposed to be solids at room temperatures, but remain liquid below their solidification (freezing) temperatures. Bisphenol A di-glycidyl ether crystals melt at approximately 42°C. Super-cooled liquids have a natural tendency to crystallize, particularly at low(er)temperatures. Liquids super-cool because the crystallization process is very slow at room temperature and the required seed

crystals are not readily formed. Exposure to extreme cold, temperature cycles and other factors may induce crystal growth and cause the materials to revert to their natural solid state.

Crystallization of epoxy resins or formulations is typically an inconvenience rather than a problem. Increasing the temperature of liquid bisphenol A based epoxy resins to 50°C (throughout the container) for a few hours will re-melt the resin. For bisphenol F based liquid epoxy resin, a temperature of about 70°C is required. This additional stage has to be accounted during formulation design because if epoxy precursor and curing agent are premixed, the warming homogenization stage has to be realized avoiding a preliminary polymerization.

Table 3 - DER331™ DGEBA resin properties (supplied by Dow Chemicals)[3]

| **Property** | **Value** | **Method** |
|---|---|---|
| Epoxide Equivalent Weight (g/eq) | 171 – 175 | ASTM D-1652 |
| Epoxide Percentage (%) | 24.6 – 25.1 | ASTM D-1652 |
| Epoxide Group Content (mmol/kg) | 5710 – 5850 | ASTM D-1652 |
| Colour (Platinum Cobalt) | 75 Max. | ASTM D-1209 |
| Viscosity @ 25°C (mPa·s) | 4000 – 6000 | ASTM D-445 |
| Hydrolysable Chloride Content (ppm) | 300 Max. | ASTM D-1726 |
| Water Content (ppm) | 700 Max. | ASTM E-203 |
| Density @ 25°C (g/ml) | 1.16 | ASTM D-4052 |
| Epichlorohydrin Content (ppm) | 5 Max. | DowM 101321 |
| Shelf Life (Months) | 24 | |

Another way to prevent crystallization is to mix different precursors. Liquid epoxy resin blends based on a combination of bisphenol A and bisphenol F epoxy resins have a demonstrated track record as having a very low tendency to crystallize. These liquid epoxy resins offer excellent resistance to crystallization and a lower viscosity versus the standard bisphenol A liquid epoxy resins. The presence of bisphenol F

epoxy resins, on the other hand, decrease the viscosity, then its use has to be assessed by accounting the process parameters needed.

The presence of water as impurities, is another key parameter, which can affect final properties of the polymerized material. Water cause hydrolyzation of epoxy ring, then can unbalance the stoichiometric ratio between reactants and lead to a product with different final properties.

### *3.3.2 Selection of Curing Agents*

The selection of curing agents is just as critical as the selection of resins. As discussed in the chapter above, there are numerous types of chemical reagents that can react with epoxy resins. Commercially, epoxy resins are predominantly cured with co-reactive curing agents: epoxy ring can be subjected to nucleophilic reactions by electrophiles and co-monomer additions take place. For thermoset epoxy resins, since co-reactive curing agents become part of the network structure, careful consideration must be paid to their contributions. Besides affecting viscosity and reactivity of the formulation, co-curing agents determine both the types of chemical bonds formed and the functionality of the cross-link junctions that are formed. Several authors have attempted to rationalize the curing agent selection process for different applications, in Table 4 are reported the main classes of co-curing agents and Table 5 show performance examples of a liquid DGEBA epoxy resin cured with some different curing agents, which can be useful for our application.

The effect of hardener structure on heat resistance of a cross-linked DGEBA resin is essential, DGEBA structure offer, typically, always an higher thermal resistance. Thermal stability is affected by the structure of the hardener. The heat resistance of aliphatic amine cured epoxy is low as measured by TGA. The nitrogen atoms are oxidized by atmospheric oxygen to amine oxides, which attack the polymer backbone. Anhydride systems tend to split off the anhydride at temperatures well below their decomposition point at about 390°C. The ether segments formed by phenolic cured epoxies have the highest thermal stability.

**Primary and secondary amines** and their adducts are the most widely used curing agents for epoxy resins. The number of amine hydrogen atoms present on the molecule determines the functionality of an amine. A primary amine group, one which has two hydrogens bound to it, will react with two epoxy groups while a secondary amine will react with only one epoxy group. A tertiary amine group, which has no active hydrogen, will not react readily with the epoxy group, but will act as a catalyst to accelerate epoxy reactions. Reactions of a primary amine with an oxirane group or an epoxy resin are shown in the following Figure 11. This type of reaction scheme involve the production of molecules having secondary hydroxyl groups. These groups are reactive with epoxy rings, then they are little competitive with amines. This aspect has to be accounted into stoichiometric global balance.

Amines are useful for create cross-linked networks between epoxidized molecules, because of their high functionality number. Then they are not valuable for obtain linear or grafted, but never cross-linked polymers, even if its reaction scheme is very efficient and selective.

Table 4 - Most used co-curing agent for epoxy resins

| **Type** | **Advantages** | **Disadvantages** | **Major applications** |
|---|---|---|---|
| *Aliphatic amines and adducts* | Low viscosity; T ambient cure; little color; low cost | Short pot life; rapid cure; critical mix ratio; moderately toxic; high moisture absorption; blush; carbonation; limited high T performance (<100◦C) | Flooring; civil engineering; marine and industrial coatings; adhesives; small castings |

| | | | |
|---|---|---|---|
| *Cycloaliphatic amines* | Low viscosity; long pot-life; room T cure and heat-curable; adhesion; good color; low toxicity; good electrical, mechanical, thermal properties (high Tg) | Slower reactivity; high costs | Flooring; paving; aggregate; industrial coatings; adhesives; tooling; composites; castings |
| *Aromatic amines* | Excellent elevated T performance (150◦C); good chemical resistance; long pot life; low moisture absorption | Solids; incompatibility with resins; long cure cycles at high T (150◦C); toxicity | High performance composites and coatings; adhesives; electrical encapsulation |
| *Polyamides* | Good mix ratios; pot life; RT cure; good concrete wetting; flexibility; low volatility and toxicity | High viscosity; low T performance; poor colour; higher cost | Marine and maintenance coatings; civil engineering; castings; adhesives |
| *Anhydrides* | Low exothermic; good thermal (high Tg), mechanical, electrical properties; low shrinkage and viscosity; long pot life; little color | Long cure cycles at high temperature (200◦C) | Composites; castings; potting; encapsulation |
| *Carboxylic-terminated polyesters* | Good weatherability, corrosion resistance, and mechanical properties; low cost | Poor chemical resistance | Powder coatings |
| *Dicyandiamide* | Good electrical properties; high temperature resistance; latent systems | Incompatibility with epoxy resins | Electrical laminates; powder coatings; single-package adhesives |

| | | | |
|---|---|---|---|
| *Phenol–formaldehyde, novolacs* | Good chemical resistance, electrical properties, shelf stability, and compatibility with epoxies; high T resistance | High melting solids; high temperature cure; poor UV stability | Moulding compounds; powder coatings; electrical laminates |
| *Phenol–formaldehyde resoles* | Stable one-component systems; excellent chemical resistance | High temperature cure; brittle; gold colour | Baked enamels; drum and pail coatings; high temperature service coatings |
| *Catalytic* | Long pot life; high temperature resistance | Brittle; moisture-sensitive | Adhesives; prepregs; electrical encapsulation; powder coatings |

Table 5 - Typycal properties of DGEBA resin (185EEW) cured with common hardeners (Dow Chemical data)[2]

| | **Curing agent** | | | | |
|---|---|---|---|---|---|
| | TETA[a] | MDA[b] | Polyamide[c] | Anhydride[d] | BF3–MEA[e] |
| phr[f] | 13 | 26 | 43 | 87.5 | 3 |
| Formulation viscosity, Pa · s (°C) | 2.25 (25) | 0.110 (70) | 1.25 (50) | 0.038 (80) | 0.040 (100) |
| Cure schedule, h (°C) | 16 (25)<br>3 (100) | 16 (55)<br>2 (125)<br>2 (175) | 16 (25)<br>3 (100) | 4 (100)<br>4 (165)<br>16 (200) | 4 (100)<br>16 (150) |
| Heat distortion temperature, °C | 111 | 160 | 101 | 156 | 168 |
| Strength, MPa | | | | | |
| Compression | 112 | 116 | 85.6 | 126 | 114 |
| Flexural | 96 | 93 | 67 | 97 | 100 |
| Tensile | 79 | 70.4 | 57.3 | 69 | 39.4 |
| Modulus, GPa | | | | | |
| Compression | 3.05 | 2.6 | 2.6 | 3.04 | 2.3 |
| Flexural | 3.05 | 2.7 | 2.14 | 3.05 | 3.1 |
| Textile elongation,% | 4.4 | 4.4 | 3.9 | 2.5 | 1.6 |

| | | | | | |
|---|---|---|---|---|---|
| Resistivity at 25°C, $10^{-17}\Omega\cdot m$ | | | | | |
| Volume | 6.1 | 12.2 | 12.2 | 6.1 | 8.6 |
| Surface | 7.8 | *>7.9* | 5.5 | *>7.3* | *>7.9* |

[a] Triethylenetetramine.

[b] 4,4_-Methylenedianiline.

[c] Versamide 140 (Henkel Corp.).

[d] Methylbicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride catalyzed with 1.5 phr benzyldimethyl-amine.

[e] Methylethylamine.

[f] Parts per hundred epoxy resin.

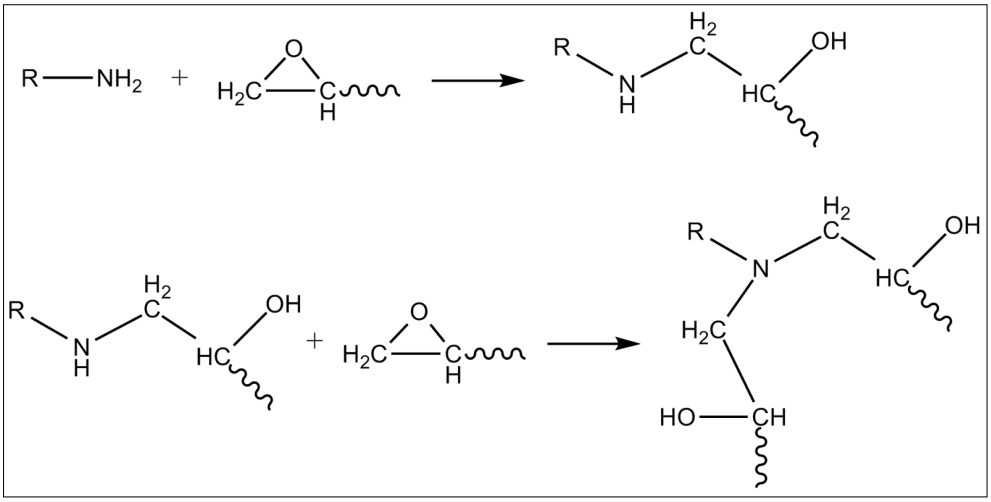

Figure 11 - Reactions of a primary amine with an epoxy group

Carboxylic polyesters and anhydrides are the second most important class of epoxy curing agent.

**Polyesters** have been growing rapidly in powder coatings formulations with epoxy resins, consuming the highest tonnage of epoxy curing agents. This is driven in part by the conversion to the more environmentally friendly powder coating technologies, and in part by the versatility and cost efficiency of polyester–epoxy hybrid powder coatings. The reaction of polyacids with polyalcohols produces polyesters. The terminal functionality is dictated by the ratio of the reactants. By virtue of their relatively cheap, widely available raw materials and good flexibility

and weatherability, acid functional polyesters are used in hybrid epoxy powder coatings for a wide range of applications. The curing mechanism of epoxy–polyester thermosets involves reaction of the acid functionality with epoxy followed by esterification of the epoxy hydroxyl groups with the acids[4] (Figure 12). Compounds such as amines and phosphonium salts catalyze these reactions. Water is a condensation reaction by-product that must be allowed to escape during the curing process to avoid coating defects.

Commercially there are a large number of polyacids, typically solid at RT, some can be easily melted and homogenized with epoxy resin to be processed via a liquid reactive processing. The strong restriction to its use is the formation of water as by-product during polymerization, which has to be removed, otherwise final polymer performance are compromised. The reactive processing is an in-bulk process and the production of by-products has to be strictly avoided. Polyalcohols, instead, can represent a better choice for our application, because reaction between epoxy and hydroxyl groups don't generate unwanted by-products. In any case, only bi-functional polyalcohols can be used, in order to prevent cross-linking phenomena.

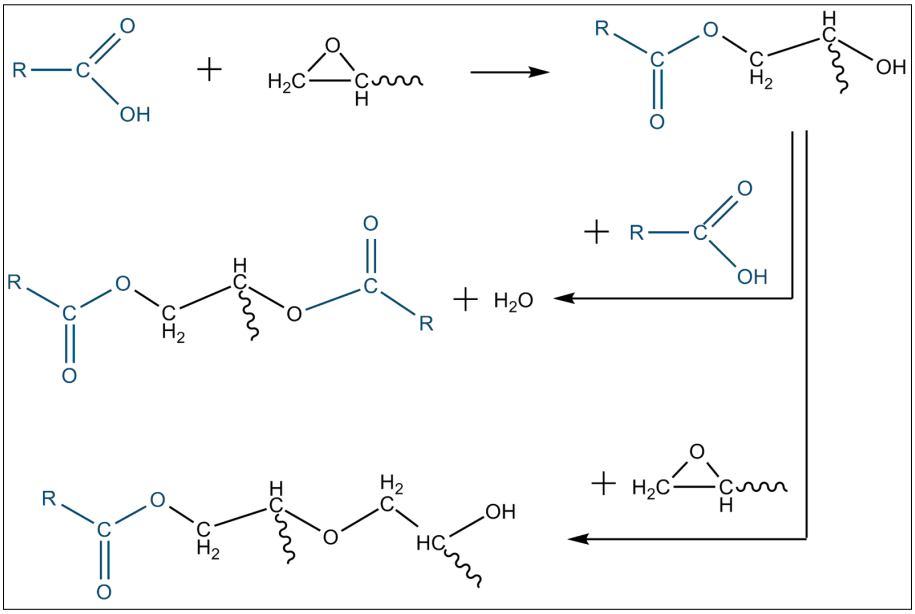


Figure 12 - The curing mechanism of epoxy–polyester thermosets

**Anhydrides** have been successfully replacing more toxic aromatic amines in composites. They are some of the very first epoxy curing agents used, and they remain a major class of curing agents used in heat-cured structural composites and electrical encapsulation, by accounting for 70% of the volume of curing agents used. While the carboxylic-terminated polyesters find widespread uses in coatings, anhydride use in coatings is minimal. Epoxy–anhydride systems exhibit low viscosity and long pot life, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The low exothermic heat generation is a unique attribute of anhydrides, making them suitable for uses in large mass epoxy cures. Curing is slow at temperatures below 200°C and is often catalyzed by Lewis bases or acids. Post-cure is often needed to develop optimum properties.

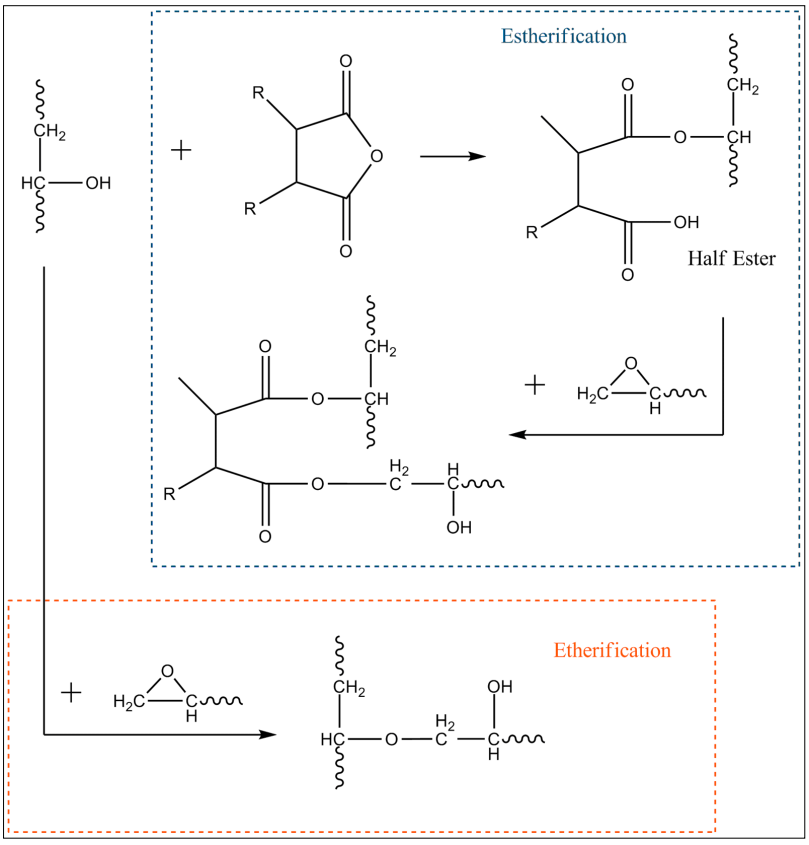


Figure 13 - Reaction of epoxy resins with acid anhydrides, esterification and etherification

Tertiary amines such as benzyldimethylamine, dimethylaminomethylphenol, boron trihalide amine complexes, stannic chloride, ammonium salts, phosphonium salts,

and substituted imidazoles are effective catalysts. Proper catalyst concentration (0.5–2.5% of resin weight) is critical, depending on the types of anhydrides and resins used and the cure schedules, and is known to affect high temperature performance. Cured epoxy–anhydride systems exhibit excellent thermal, mechanical, and electrical properties, and are used in filament-wound epoxy pipe, PCB laminates, mineral-filled composites, and electrical casting and encapsulation applications. Anhydride-cured epoxies also have better aqueous acid resistance than similar amine-cured systems. The mechanism of anhydride cure is complex and controversial because of the possibility of several competing reactions. The uncatalyzed reaction of epoxy resins with acid anhydrides proceeds slowly even at 200◦C; both esterification and etherification occur (Figure 13). Secondary alcohols from the epoxy backbone react with the anhydride to give a half ester, which in turn reacts with an epoxy group to give the di-ester. A competing reaction is etherification of an epoxy with a secondary alcohol, either on the resin backbone or that formed during the esterification, resulting in a β-hydroxy ether. It has been reported that etherification is a probable reaction since only 0.85 equivalents of anhydrides are required to obtain optimum cross-linked density and cured properties in case of formulation of thermoset epoxy polymers.

Just for their multiple reaction scheme anhydrides are not the ideal co-reactive curing agent to obtain thermoplastic polymers, although performances of their final products are remarkable.

**Phenolics** form a general class of epoxy curing agents containing phenolic hydroxyls capable of reacting with the epoxy groups. They include phenol-, cresol-, and bisphenol A terminated epoxy resin hardener. More recent additions include bisphenol A based novolacs. Cure takes place at elevated temperatures (150–200◦C) and amine catalysts are often used. The bisphenol A terminated hardeners are produced using liquid epoxy resins and excess bisphenol A in the resin advancement process. They are essentially epoxy resins terminated with bisphenol A. They are popular in epoxy powder coating applications for rebar and pipe, providing more flexible epoxy coatings than the novolacs. The novolacs are

produced via the condensation reaction of phenolic compounds with formaldehyde using acid catalysts. They are essentially precursors to epoxy novolacs. Novolacs are multifunctional curing agents and can impart higher cross-link density, higher Tg, and better thermal and chemical resistance than other phenolics. Cresol novolacs provide higher solvent and moisture resistance, but are more brittle than their phenol novolac counterparts. Recently, bisphenol A based novolacs have been used in electrical laminate formulations to improve thermal performance (Tg and Td). Novolacs are widely used in composites, PCB laminates, and electronic encapsulation applications. Their uses in coatings are limited to high temperature applications such as powder coatings for down-hole oil-field pipe coatings. The reaction scheme with epoxy rings is represented inFigure 14.

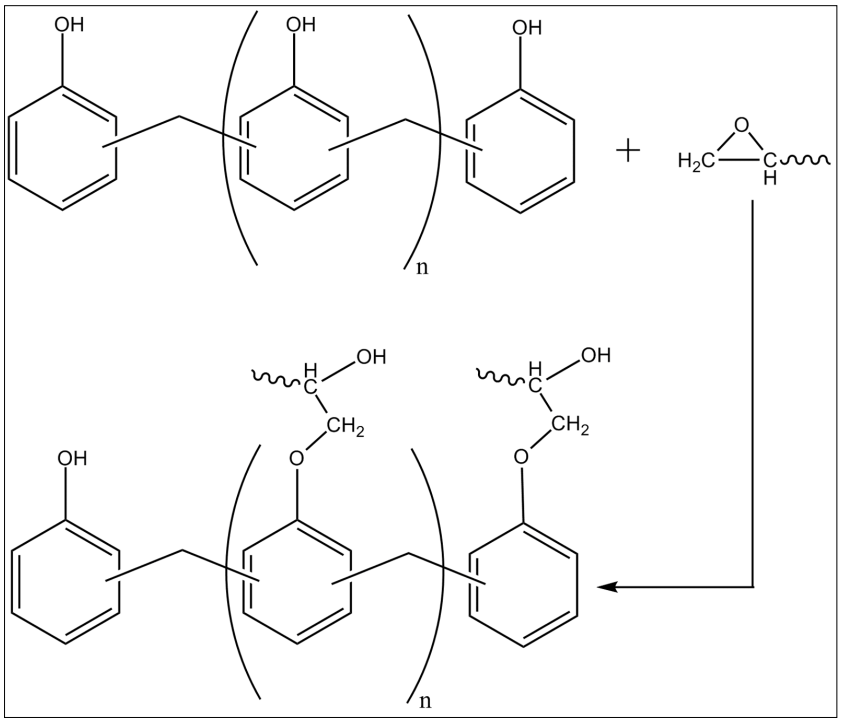


Figure 14 - Reaction of poly-phenols with epoxy rings

In the same way of polyalcohols, reaction between epoxy and hydroxyl groups don't generate unwanted by-products, and the use of bi-functional phenolics can, effectively, prevent high cross-linking levels, and linear polymer chain growth is favourite. Then bisphenols one of the better choice to obtain thermoplastic epoxy-based polymer by reactive processing. The choice of the type of bisphenol co-

monomer depends mainly by the chemo-rheological properties of the reactive mixture. The choice of high molecular weight precursors to reach high mechanical and thermal final properties stands in the way of ensure the reactive process feasibility and the improved coupling with reinforcement in composite applications. Regarding, also, to a cost effective solution, the use of bishenol A as co-reactive monomer can be an optimal choice.

### *3.3.3 Epoxy/Curing Agent Stoichiometric Ratios*

In addition to the choices of epoxy resins and curing agents, the stoichiometric ratio of epoxy/curing agent is another factor that has significant effects on the structure and final performances. A variety of products can be obtained from different ratios. As an example in thermoset formulation a typical case is the network formation for a di-functional epoxy resin and a tetra-functional amine. The products range from an epoxy–amine adduct with excess epoxy to an amine–epoxy adduct with excess amine. Theoretically, a cross-linked thermoset polymer structure is obtained when equimolar quantities of resin and hardener are combined. However, in practical applications, epoxy formulations are optimized for performance rather than to complete stoichiometric cures. This is especially true when curing of high MW epoxy resins through the hydroxyl groups. In primary and secondary amines cured systems, normally the hardener is used in near stoichiometric ratio. Because the tertiary amine formed in the reaction has a catalytic effect on reactions of epoxy with co-produced secondary alcohols, slightly less than the theoretical amounts should be used. However, if substantially less than the theoretical amount of amine is used, the epoxy resin will not cure completely unless heat is applied (post-cure). The use of excess amine will result in unreacted amine terminated dangling chain ends and reduced cross-linking, yielding a polymer that can be somewhat tougher but which is considerably more susceptible to attack by moisture and chemicals.

In formulations containing anhydrides, less than stoichiometric ratios of curing agents normally are used (0.50 to 0.85 of anhydride to 1 epoxy stoichiometric ratio) because of significant epoxy homopolymerization. Ladder studies are often conducted varying the stoichiometric ratios and other factors to determine the

optimum formulations. Information concerning network structures can be obtained using dynamic mechanical analysis (DMA) and chemo-rheology to guide formulation development[5].

In the case of bi-functional DGEBA, with a lower number of polymerization, reacting with bisphenols the ideal condition is the 1:1 stoichiometric ratio. During polymerization process the formation of hydroxyl groups takes place, then epoxy activated rings can react also with it. Then a slight unbalanced stoichiometric ratio (~0.95 for example) can account this eventuality and limiting the over cure and the formation of densely cross-linked macromolecules, which will not exhibits thermoplastic behaviour.

### *3.3.4 Catalysts*

The catalytic curing agents are a group of compounds that promote epoxy reactions without being consumed during the process. The choice of a catalyst and of its amount is important. In the epoxy literature, catalysts are referred to as "accelerators" and, according to Lewis theory, are divided in acid and bases. Lewis bases contain an unshared pair of electrons in an outer orbital and they attempt to react with areas of low electron density. They act as nucleophilic catalytic curing agents for epoxy homopolymerization, as co-curing agents for primary amines, polyamides, and amidoamines and as catalysts for anhydrides and phenols. As discussed in previous sections, some tertiary amine catalysts can play multiple roles in the curing reaction and some co-reactive agents, like anhydride of phenolics, are highly sensitive to catalyst amount. Nucleophilic catalysts, used with acidic curing agents such as anhydrides and novolacs, can greatly reduce the gel time. Imidazoles are more efficient accelerators than tertiary amines; only half the concentration is required to produce the same catalytic effect. In case of reactive processing these epoxy matrices are in-situ reacting systems and they require custom-made catalysts to ensure the maximum chemical conversion within the allowed processing windows. In our case, DGEBA resin will react with bisphenols, then epoxy rings has to be activated.

Several kind of chemicals were tested as catalyst for the DGEBA based system: a tertiary amine and an alchidic ammonium/phosphonium salts[6]. Tertiary amines are commonly used as catalyst, but, due to its volatility and toxicity, handling may lead to unsafe working conditions compared to alchidic salts. Conversely, alchidic salts, classified as much less toxic chemicals, may be reasonable substitutes; nevertheless, being solid at room temperature, they lead to more inconveniences during the homogenization process within an epoxy resin. An efficient mixing procedure was set up and the curing behaviour was investigated by Differential Scanning Calorimetry (DSC) in order to study the kinetics evolution.

Tertiary amines are the most commonly used as nucleophilic catalysts. The rate of cure of epoxy resins with tertiary amines depends primarily upon the extent to which the nitrogen is sterically blocked. Quaternary ammonium or phosphonium salts have been used as fast catalysts for curing of phenolics, carboxylic acid-terminated polyesters, or anhydrides with epoxies in powder coatings formulations, they showed good latency and fast cure rates at moderate temperatures. For both catalysts several different mechanisms are possible but all reactions are based on the ring opening of the epoxy moiety by catalyst action, except for anhydrides, which are directly activated by tertiary amines.

The catalytic curing reactions of tertiary amines with epoxy resins follow two different pathways, depending on the presence or absence of hydrogen donors, such as hydroxyl groups. In the absence of hydrogen donors, tertiary amines react with the electron-poor methylene carbon of the epoxy group to form an intermediate zwitterion. With more acidic hydrogen donors such as benzyl alcohol, phenols, or mercaptans, the tertiary amine acts as a co-curing agent by first abstracting the proton from the hydrogen donor. The proposed reaction schema is reported in Figure 15.

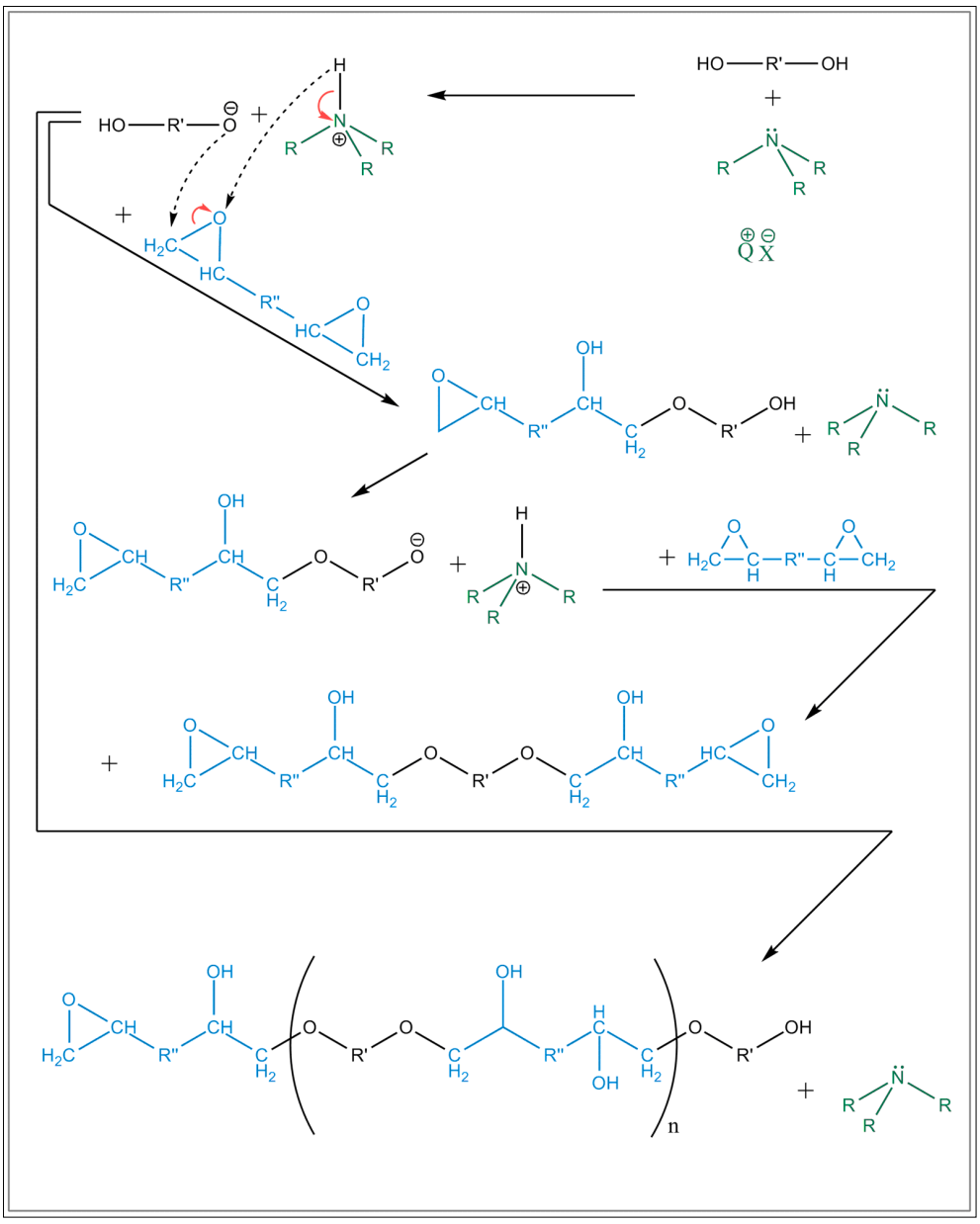

Figure 15 – Tertiary amine: proposed reaction schema for a bisphenol-DGEBA system

Quaternary ammonium or phosphonium salts ($Q^+ X^-$) promote polymerizations of bisepoxides with bisphenols in hot etheric solvents[7, 8] or in the melt to produce poly(hydroxyl)ethers, which can provide homopolymers, alternating copolymers or random co - and terpolymers, depending upon the choice and variety of bisphenols and diepoxides utilized in the polymerization.

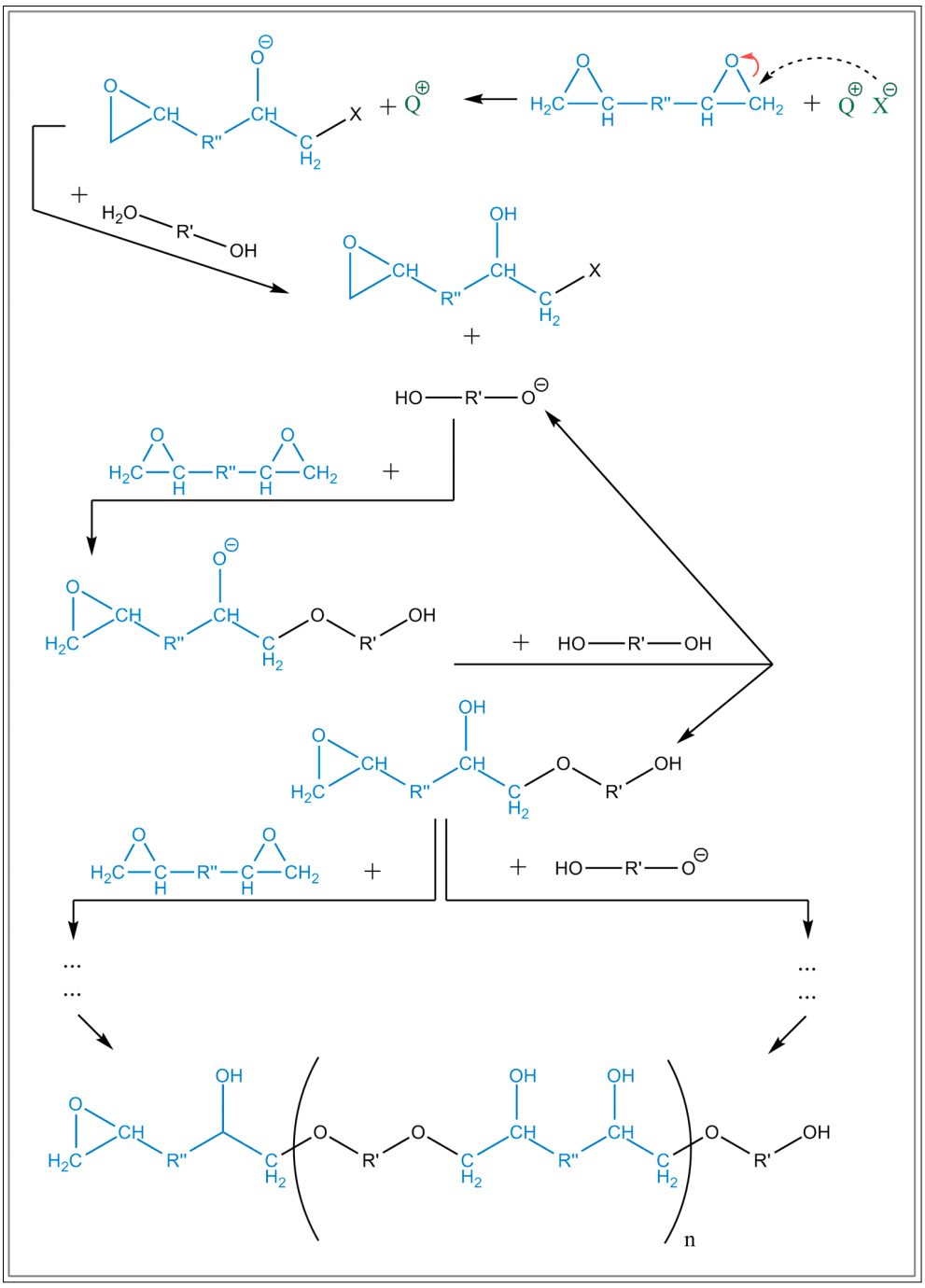

Figure 16 – Alchidic ammonium/phosphonium salt: proposed reaction schema for a bisphenol-DGEBA system

Basically, the reaction is based on nucleophilic ring opening of the epoxy moiety by phenate, but the polymerization pathway is more complex than it might seem at first glance. Stoichiometrically, the reaction behaves like a classical step-growth

process; in other words, the molecular weight increases geometrically with monomer conversion, and an equimolar ratio of reactants is necessary to produce products with high molecular weight. However, the polymerization also has characteristics of a chain process, in which the anionic component ($X^-$) of the quaternary salt (basically acting as an initiator) attacks an epoxy functionality to yield alkoxide, which deprotonates a phenolic species to give a nucleophilic phenate and hydrin. Reaction of phenate with an unconsumed epoxy group gives intermediate, which can be neutralized by unreacted phenolic end groups forms hydroxy phenoxy linkage, which is the basic backbone unit of polymers. Polymerization propagates, essentially, by regenerating phenate that continue to react with remaining epoxides until phenolic and epoxy end groups are completely exhausted or until side reactions terminate growth of the polymer chain (Figure 16).

A tertiary amine allows an easy and efficient mixing as the resin batch could be achieved by using a standard procedure. On the other hand, alchidic salts, solid at room temperature, require a preliminary homogenization stage in a small amount of epoxy in order to obtain a stable paste. For each considered catalyst three different concentration were prepared, namely (0.5%wt, 1%wt and 3%wt).

Thermo-calorimetric (DSC) analysis was carried out and under dynamic conditions (heating rate 10°C/min). Figure 17 and Figure 18 show the DSC experimental data for each concentration, respectively, of tertiary amine and ammonium salt. In the case of the tertiary amine, the lower concentration (0.5%wt) limits significantly the conversion grade (significantly lower reaction enthalpy). The ammonium salt have shown comparable results with the tertiary amine: in fact, reaction heat is substantially the same and curing peaks are shifted slightly to higher temperatures. This shift is useful to prevent unwanted pre-polymerization during fibre impregnation stage in the fibre reinforced composite manufacturing.

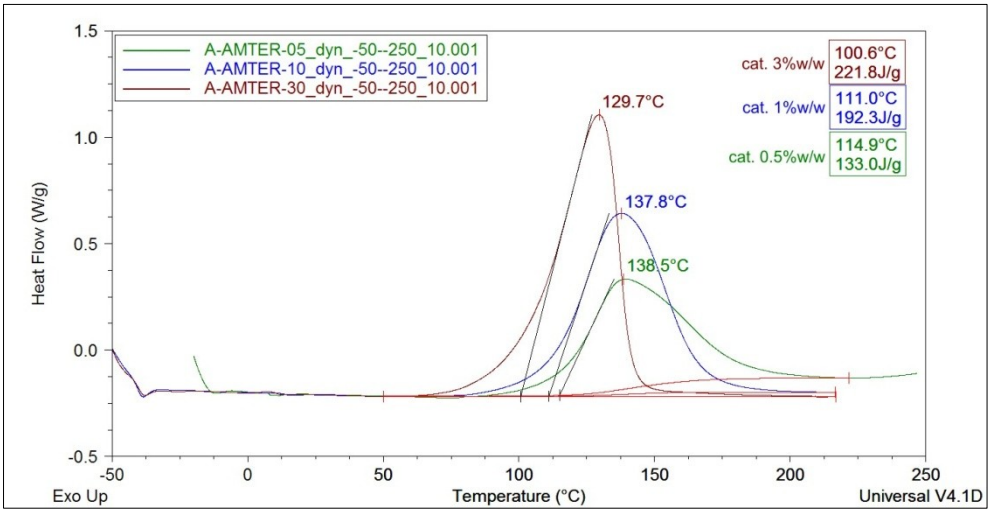


Figure 17 – Catalyst effect of a tertiary amine on DGEBA/Bisphenol system at different concentration (0.5 % wt , 1 % wt and 3 % wt )

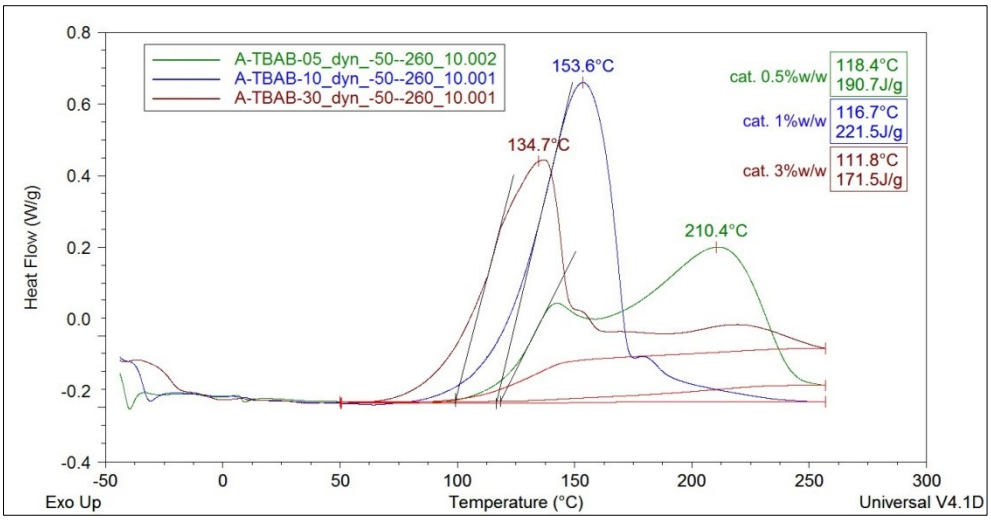


Figure 18 - Catalyst effect of an ammonium alchidic salt on DGEBA/Bisphenol system at different concentration (0.5 % wt , 1 % wt and 3 % wt )

Figure 19 reports for a batch catalyzed using less than 1%wt concentration of salt the dynamic polymerization curves at various heating rates (3,5,10°C/min). By increasing the heating rate an enthalpy peak shift occurs ($T_{peak}$=153-165°C), but temperatures are fully compatible with standard process parameters for manufacture reinforced composite by reactive processing (100-180°C). Reaction enthalpy release occurs significantly near 100°C ($T_{onset}$=103-115°C), then the polymerization stage has to be conducted at higher temperatures. On the other

hand, all preparation procedure for blend reactive precursor and reinforcement materials has to be realized at lower temperatures, to prevent unwanted pre-polymerizations. Reaction enthalpy measures ($\Delta H_{cure}$=215-265 J/g), reach the maximum level at 5°C/min heating rate, which is compatible with industrial standard process parameters.

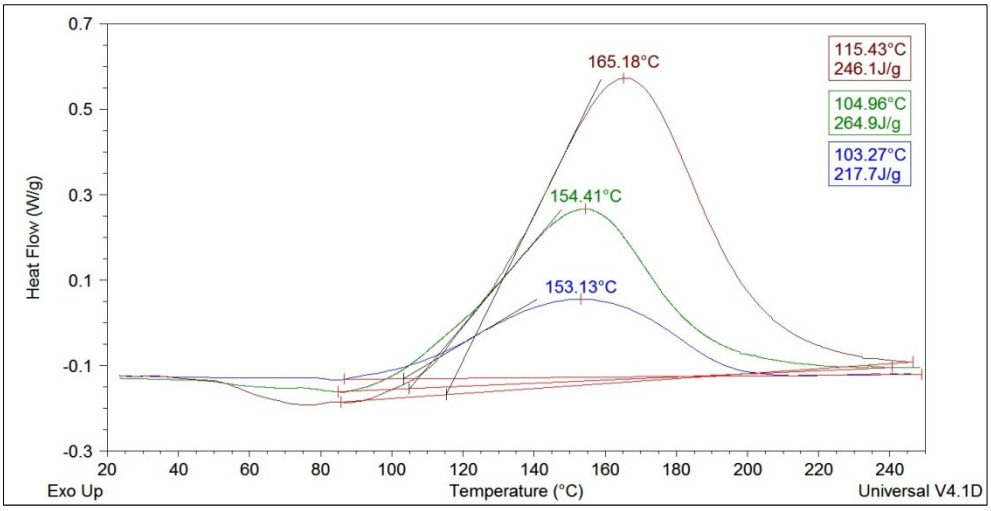


Figure 19 – Reaction enthalpy of DGEBA/Bisphenol system

All catalyst (tertiary amine and ammonium salt) can be efficiently used as accelerators for liquid epoxy systems normally used to manufacture fibre reinforced polymer composites. A standard procedure can be employed to produce resin batches by using amines while a pre-stage mixing is required in the case of alchidic salt. Although alchidic salts require higher curing temperature to achieve full conversion grade, on the other hand they allow a safer handling process and the capability to expand the processing window.

### *3.3.5 Accelerators*

Accelerators are commonly added to epoxy systems to speed up curing. This term should be used to describe compounds which increase the rate of catalyzed reactions but which by themselves are not catalysts. However, the term accelerator is often used synonymously with catalyst in some of the literature. Hydrogen donors such as hydroxyl groups facilitate epoxy reactions via hydrogen bonding or reaction

with the oxygen on the epoxide ring. More acidic donors such as phenols and benzyl alcohols increase the rate of acceleration. However, very strong acids can interfere with amine curing agents by protonation of the amine to form an amine salt, resulting in increased pot life. Figure 20 shows the effects of different accelerators on the rate of a DGEBA/triethylenetriamine formulation.

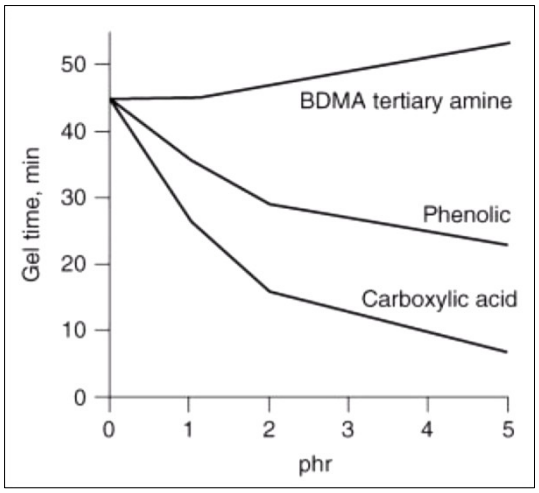


Figure 20 - Effects of accelerator on epoxy/triethylenetriamine cure[2]

In our case bisphenols already present in the reactive mixture as co-monomers play a role of accelerator. In opposition the presence of an high quantity of bisphenols can speed up excessively the polymerization process and reduce the processing window. Then the reaction velocity has to be controlled, with catalyst amount and processing temperature.

## 3.4 Epoxy Polymerization Process

The epoxy polymerization represents a fundamental stage of the overall manufacturing process which indeed will affect the final performances of the cured material system. For this reason, it become imperative to analyse and to understand the different curing and kinetics evolution steps in order to achieve an optimal level of performance in the final composite. Excellent reviews on this topic are available in the literature[9, 10], but they are mainly limited to thermosetting epoxy polymers.

The curing of a thermoset epoxy resin can be expressed in terms of a time–temperature-transformation (TTT) diagram, see Figure 21[11]. In the TTT diagram, the time to gelation and vitrification is plotted as a function of isothermal cure temperature.

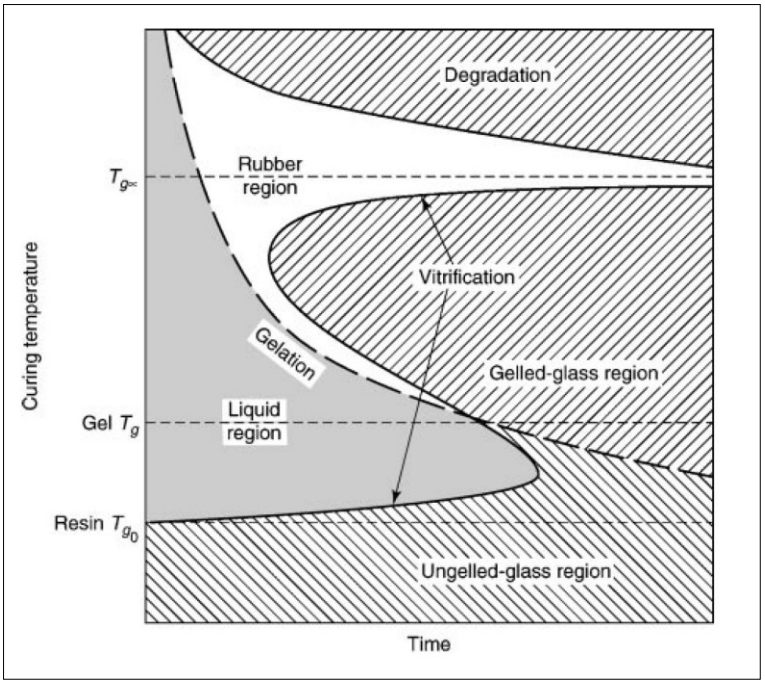


Figure 21 - TTT Diagram for a thermosetting epoxy reactive system

The main features of TTT diagram are: gel point and onset of vitrification. The gel point is defined as the onset of the formation of insoluble, cross-linked polymer (gel fraction) in the reaction mixture. However, a portion of the sample may still be soluble (sol fraction). The onset of vitrification is when the glass-transition temperature (Tg) of the curing sample overcomes the curing temperature Tc. Ideally, a useful thermosetting system suitable for structural applications would cure until all monomers are built into the network, resulting in no soluble fraction. The S-shaped vitrification curve and the gelation curve divide the time-temperature plot into four distinct states of the thermosetting-cure process: liquid, gelled rubber, ungelled glass, and gelled glass. Tg0 is the glass-transition temperature of the unreacted resin mixture; Tg∞ the glass-transition temperature of the fully cured

resin; and gel Tg represents the point where the vitrification and gelation curves intersect.

In the early stages of cure prior to gelation or vitrification, the epoxy curing reactions are kinetically controlled. When vitrification occurs the reaction is diffusion controlled, and the reaction rate is orders of magnitude below that in the liquid region. With further cross-linking of the glass, the reaction rate continues to decrease and it is eventually quenched. In the region between gelation and vitrification (rubber region) the reaction can range from kinetic to diffusion control. This competition causes the minimum in vitrification temperature reported in the TTT diagram between gel Tg and $Tg_\infty$.

As the cure temperature is raised the reaction rate increases and the time to vitrification decreases until the decrease in diffusion begins to overcome the increased kinetic reaction rate. Eventually, slower diffusion in the rubbery region decreases the overall reaction rate and thus the increase in time to vitrify is seen. Below $Tg_\infty$, the reaction does not go to completion. As curing proceeds, the viscosity of the system increases as a result of increasing molecular weight, and the reaction becomes diffusion-controlled and eventually is quenched as the material vitrifies[12]. After quenching, the cure conversion can be increased by raising the temperature. This is often practiced as post-cure for certain epoxy systems to achieve maximum cure and performance. Post-cure is only effective at temperatures higher than $Tg_\infty$. However, it must be noted that at temperatures sufficiently above $Tg_\infty$, onset of network degradation can also be seen if sufficient time is involved. Thus one must be careful about potential "over-curing."

The TTT diagram is useful in understanding the cure kinetics, conversion, gelation, and vitrification of the curing thermoset. Gelation and vitrification times can be determined from the intersections of the storage and loss moduli and the maxima in the loss modulus of an isothermal dynamic mechanical spectrum, respectively. Recently, techniques have been developed using rheological and dynamic mechanical analysis instruments to determine the gel point and vitrification[13].

Understanding the gelation and vitrification characteristics of an epoxy/curing agent system is critical in developing the proper cure schedule/process to achieve optimum performance. One important application is the management of cure temperatures (Tc) and heating rate: if T is too low, vitrification may occur before gelation and further reactions may not be completed, resulting in an incomplete network structure and poor performance. Furthermore, attention must be paid to the relationship between mixing of reactants and gel point. Epoxy resins and curing agents must be carefully mixed prior to the gel point since the rapid viscosity build-up at gel point inhibits homogeneous mixing of reactants, resulting in potential network and morphological inhomogeneities and defects.

The material developed during this work will be thermoplastic, then the TTT diagram as reported above it's not useful for well represent the polymerization phenomena. TTT diagram for thermoset system mainly provides the processing conditions (temperature and time) to reach gelation of whole polymer mass before vitrification occurs. If the materials behave as a thermoplastic system chemical gelation, due to cross-linking, does not occur. Macromolecules generated by reaction are linear or ramified, slightly cross-linked, and they arrange in networks in which bonds between polymer chains are weak and temperature sensitive. Then this "physical gel" condition can be modulated by varying temperature. Using this feature the reaction rate can be tuned by switching between kinetically controlled and diffusion controlled phases, by control the processing temperature.

In the early stages of cure, the system is in its liquid region and reactions are kinetically controlled. In this phase, the first polymerizations among bisphenols and epoxy molecules activated by catalyst are realized. These chemical conditions are ideal as unwanted collateral reactions cannot occur. In fact, etherification reactions, among activated epoxy groups and hydroxyls, formerly created in the polymer chain by the reaction between a bisphenol reacted and an opened epoxy ring, cannot take place. Whereas, the epoxy homopolymerization can be complied due to its contribution in linear growth of the polymer chains. Nevertheless, homopolymerization needs to be minimized by reducing the reaction temperature,

in the first reaction stage, as it unbalances the initial stoichiometric ratio between epoxy and bisphenols. In the subsequent stages, if temperature is sufficiently high and the formed macromolecules have high mobility, the collateral reactions can be competitive with principal polymerization.

Above consideration lead to the conclusion that the optimal conditions will be when the active epoxy can react with bisphenols and macromolecules, which have low molecular weight, through kinetically controlled mechanism. On the other hand, the same active epoxy has to react with macromolecules already formed, characterised by a medium or high molecular weight, through diffusion controlled mechanism. In this way the probability of cross-linking is reduced and forming macromolecules, before branching o cross-linking, can develop mainly linearly, reaching an adequate molecular average weight.

A simplified scheme for the proposed reaction mechanism would be a two stage polymerization process, like the cure and post-cure stage, commonly used for thermoset polymers. In the first stage, the temperature has to be sufficiently high to ensure that the entire reactive system is in its liquid region, without starting homopolymerization or branching reactions. In the second stage, the temperature is set sufficiently high to shift the system from the glassy to its rubbery state and to allow a suitable mobility for branching reaction to take place for a reduced time avoiding cross-linking phenomena.

### *3.4.1 Polymerization stages optimization*

To set up the correct temperatures and time dwell for polymerization stages, DSC e rheometric tests can provide key information.

The first rheometric test was performed on precursors mix, by excluding only catalyst. Since the catalyst is presents in a very small percentage the viscosity profile of the uncatalyzed mixture could well represent the rheological behaviour of the overall system, assuming that polymerization reaction cannot take places. The test was set up in oscillatory mode, at constant angular frequency (5rad/s) and

amplitude percentage (10%), using an heating rate of 10°C/min over the temperature range from 20°C to 200°C. Since the analysed system exhibited medium-high viscosity and the velocity field was very small, a plate-plate testing fixture could be used. In order to minimize the temperature gradient, plate diameter was 25 mm with a gap of 0.5 mm. The viscosity profile obtained is reported in Figure 22. The system exhibits an high viscosity near ambient temperature, like all commercial epoxy systems, by heating up to 80-100°C the viscosity reaches lower levels (~100mPa·s), which are fully compatible, both with manufacturing processes needs, both with requirements for a liquid polymerization in bulk. This results highlight that first stage polymerization must be performed at temperatures above 100°C.

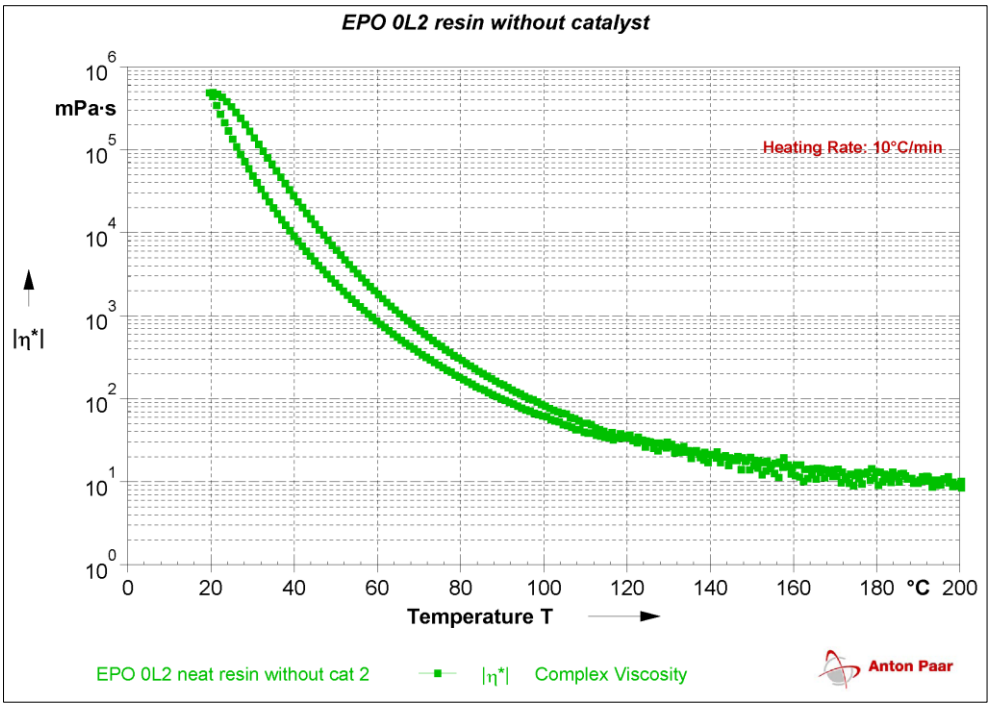


Figure 22 – Viscosity profile of reactive mixture bisphenols/DGEBA without catalyst

Calorimetric tests (DSC) were also carried out: firstly dynamic scanning at different heating rates (1,3,5,7.5,10 °C/min) within the range 25-250°C were performed, then

isothermal scanning at suitable temperatures where reaction velocity starts to be appreciable, were run.

Dynamic scans are reported in Figure 23. From dynamic test the most important information, which can be marked are:

- The polymerization takes place within the range ~90°C-250°C, with one exothermal peak, representing the reaction enthalpy.

- The reaction enthalpy ranges from 200 J/g up to 250 J/g, according to preliminary tests already made for the catalyst selection. Values monotonically increase with the heating rates: at lower heating rate, the system reacts so fast that vitrification occurs before the arising of the temperature for the system. Moreover, the global polymerization efficiency is lower and the total heat of reaction is extremely low. This latter effect is more evident up to heating rates of 5°C/min, while above the differences are minimal.

- Exothermal peaks are in the range 145°C-164°C. This is mainly due to different averaged reaction velocities, which occurs at different heating rates, due to reaction kinetics.

- Small endothermic peaks are visible near 80°C. They are essentially due to a partial phase change of precursors. Highly quality DGEBA and bisphenols tends to crystallize at room temperature, as reported above in the precursors selection section.

According to the information gathered by the dynamic DSC scans, isothermal scanning was carried out at temperatures in which reaction velocity starts to be appreciable, i.e. between 80°C and 95°C. Results are presented in the Figure 24. Tests were performed by setting a 1°C/min heating ramp from room temperature up to the required temperature (80, 85, 90,95 °C), then this temperature was hold constant for a long dwell time.

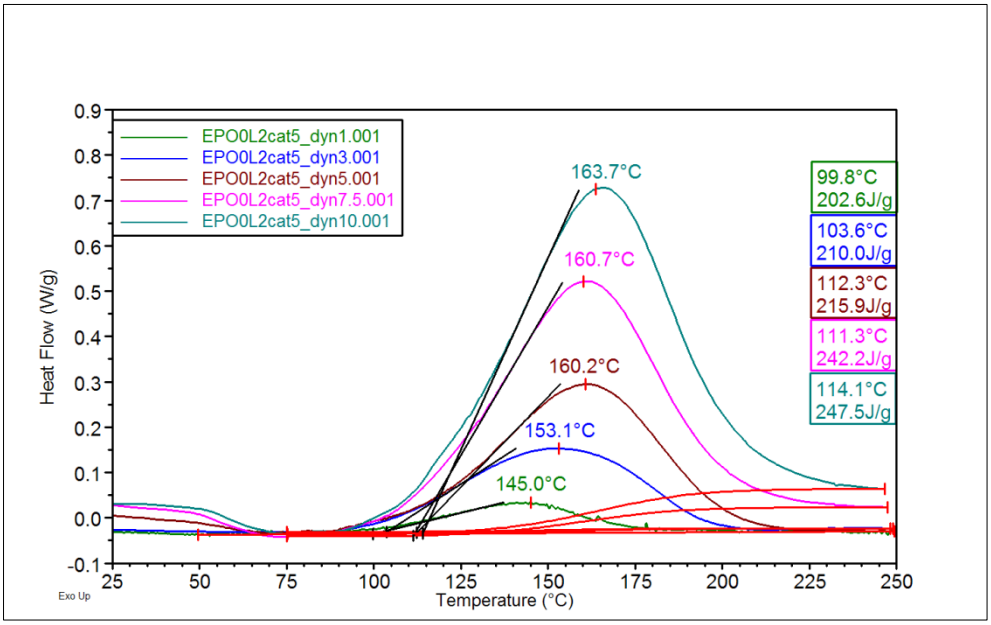


Figure 23 – Dynamic scanning at different velocities of the catalyzed bisphenols/DGEBA mixture

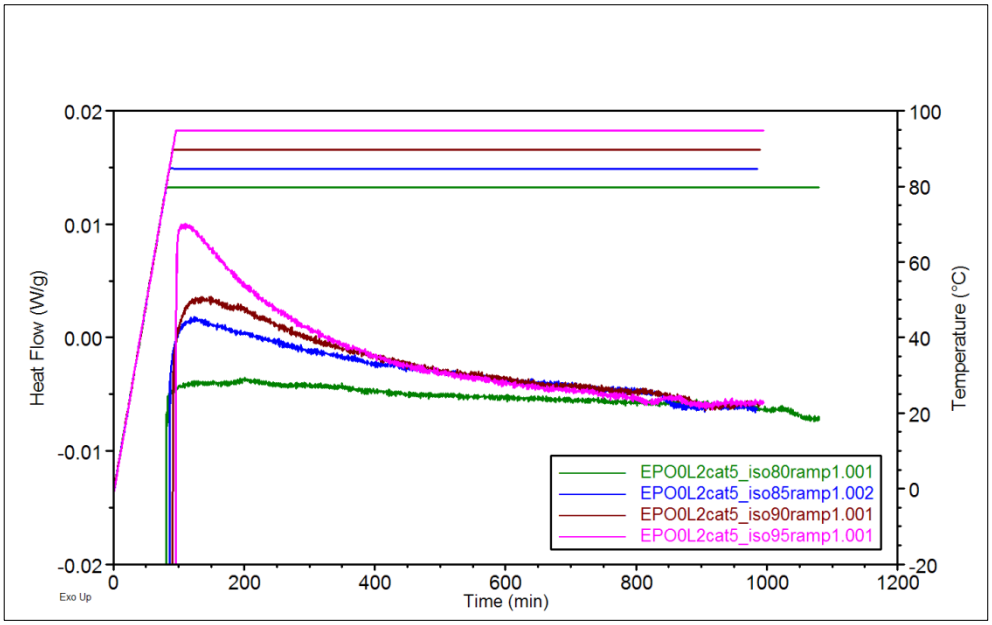


Figure 24 - Isothermal scanning at different temperatures of the catalyzed bisphenols/DGEBA mixture

Results indicates that at 80°C no chemical reaction takes place, for higher temperature the instrument reveal an heat release, the polymerization occurs at appreciable velocities, but vitrification occurs before reaction completion.

DSC results confirm that the first stage of polymerization has to be carried out at temperatures near the exothermal polymerization peak temperature, in order to take advantage from the highest reaction velocity, then it can be conducted at a temperature between 140°C and 180°C, near the exothermic polymerization peak. To prevent vitrification during the heating stage, the temperature rate is equal or higher than 5°C/min.. Indeed, under these conditions, the reactive mixture will reaches minimal viscosity level before increasing due to the cure progression.

In to setup the most suitable polymerization temperature during the first stage, rheometric test on reactive system has been carried out. Three tests was were conducted in oscillatory mode, by using the same parameters employed for the unreactive mixture. The heating ramp was set to 5°C/min and the isothermal temperature was 140, 160, 180°C, respectively. The dwell time period was set up to 2 hours for 160°C and 180°C scan and 3 hours for 140°C test. Results are reported in Figure 25.

From these tests the most important information, which can be marked out, are reported hereafter:

- at the beginning the reactive mixture behaves as the uncatalyzed system, as up to until 100°C reaction velocity are negligible compared to heating rate
- above over 100°C the polymerization occurs with an appreciable velocity. The minimum of viscosity was recorded at about 110°C (less than 0.1Pa·s). Whereas, above this temperature viscosity dramatically grows up reaching a level higher than 100Pa·s in a few minutes.
- for the test carried out at a isothermal temperature of 140°C, viscosity curve achieves a plateau in about 30 minutes leading to the conclusion that the system surely has vitrified.

- for tests carried out at isothermal temperatures of 160°C and 180°C, viscosity exhibits the same trend however, don't it won't reach the same "plateau level" throughout the all experiment. In this case, the system tends to vitrification but some reactions can take place, through a diffusion process.

These tests may offer some useful indications to set up the first stage of the optimized polymerization process. In fact, as first evidence, it can be stated that the polymerization performed at 140°C is not useful due to the early vitrification reached by the system. Whereas, the tests realized at 160°C do not show this feature.

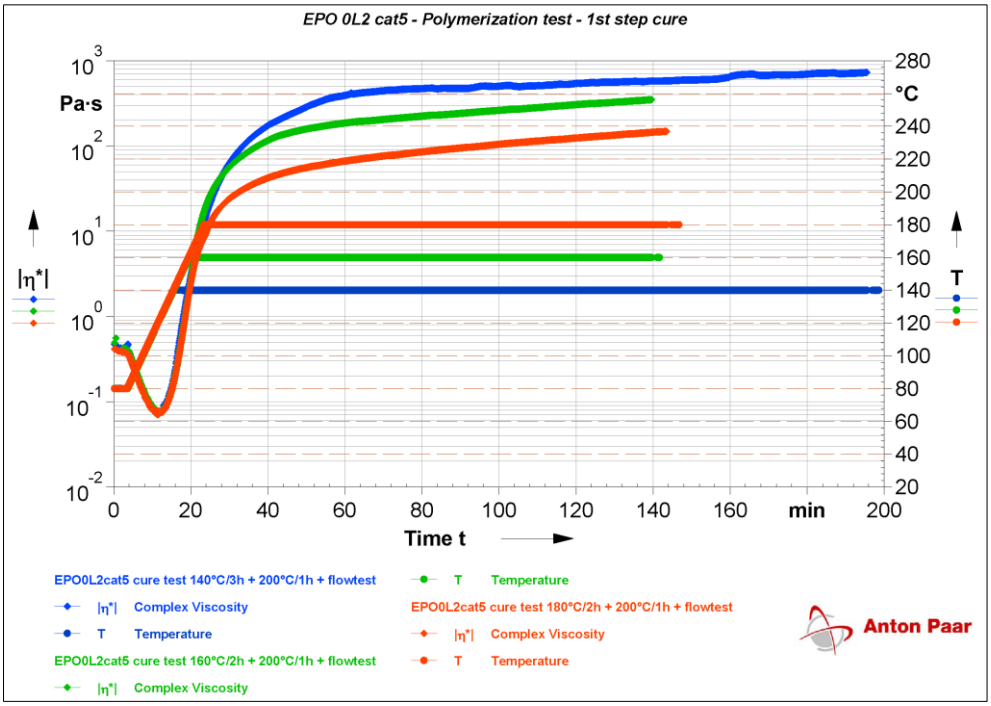


Figure 25 – Rheometric polymerization tests at different temperatures of the catalyzed bisphenols/DGEBA mixture

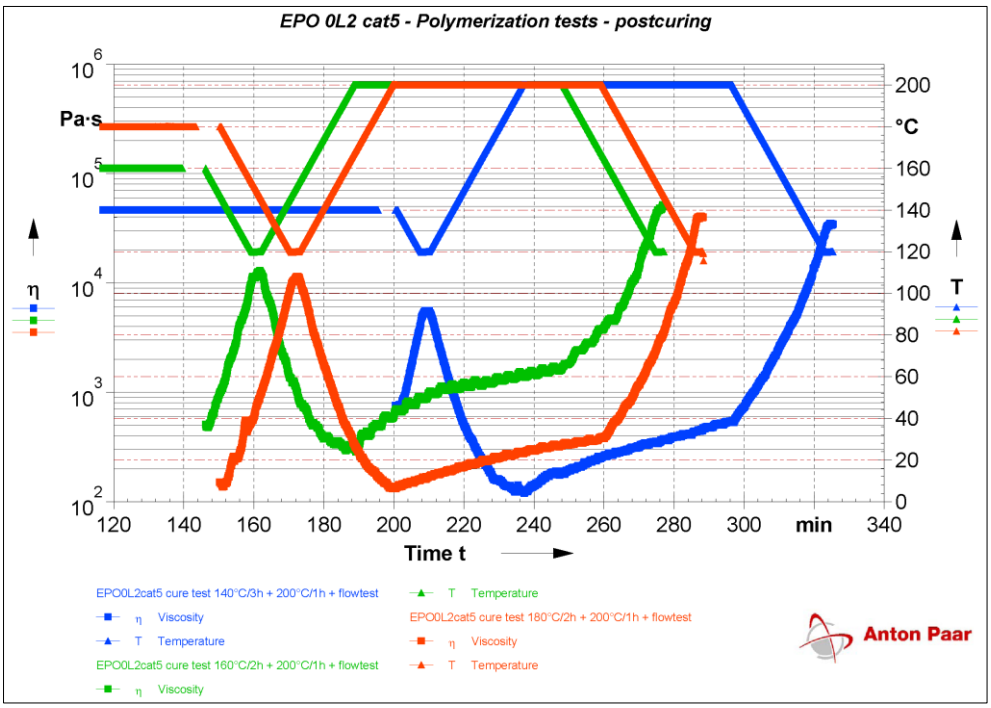


Figure 26 - Rheometric tests of the second polymerization stage of the catalyzed bisphenols/DGEBA mixture

The same samples, which have undergone a polymerization process as the one described above, have been subjected to a second curing stage, at 200°C for 1 hour, in order to reach the maximum grade of polymerization. For these latter tests, heating/cooling ramps were conducted at 3°C/min. Results are reported in Figure 26.

During the hot stage at 200°C in all samples further polymerizations took place, with an extra viscosity increasing. The sample cured in the first stage at 160°C, exhibits the higher rising, reaching a viscosity of $10^3$ Pa·s at 200°C and nearly $10^5$ Pa·s at 120°C. For all samples after 30min the vitrification condition was surely reached.

As results of the above reported rheometric test, then, the first stage of the polymerization reaction can be suitably set to 160°C by choosing an heating ramp of 5°C/min within the range 80°C-160°C. The dwell time period can be fixed at 60minto ensure the maximum polymerization level at 160°C. The second polymerization stage can be set up at 200°C for no longer than 30min.

## 3.5 Characterization of the EPO system

For sake of simplicity, the formulated thermoplastic epoxy-based reactive system has been labelled EPO from this point.

Below are summarized the most significant results for the final thermoplastic epoxy-based reactive system according to the different experimental test conducted on the system during the optimization of experimental parameters for the polymerisation procedure.

A DSC dynamic scan (10°C/min) is reported in Figure 27. Similarly to other dynamic test performed at different heating rates (see Figure 23) during the first ramp up to 250°C the polymerization reaction take place, and an exothermal peak appears.

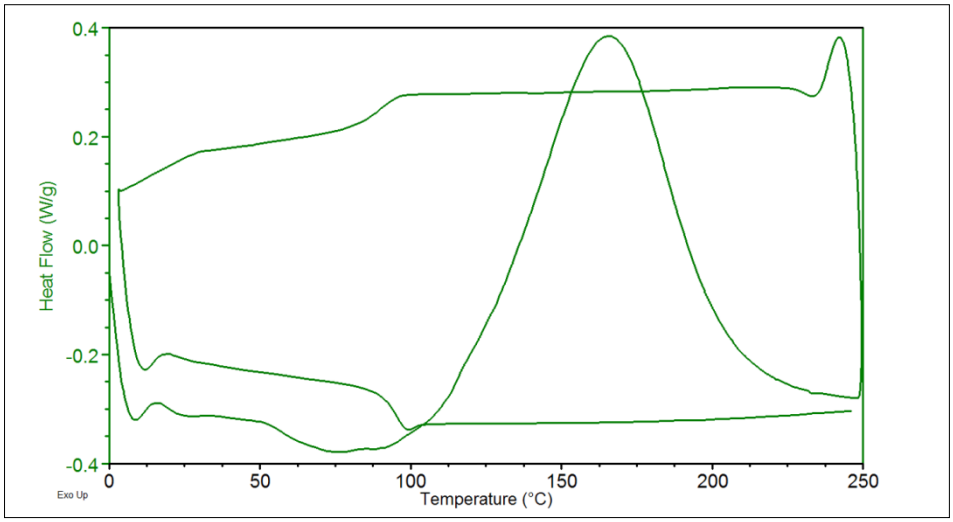


Figure 27 – Dynamic scanning at 10°C/min of EPO system

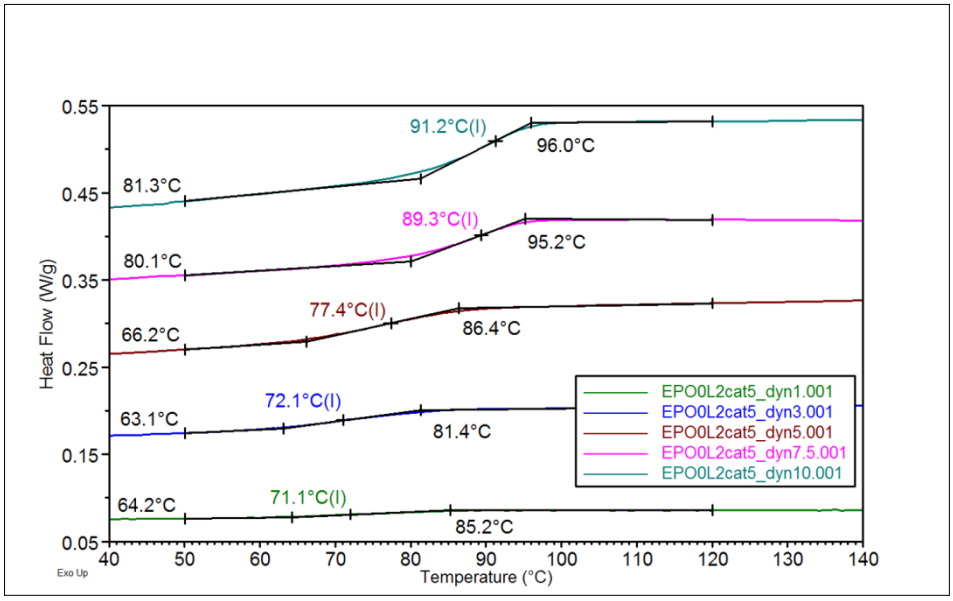


Figure 28 – Glass transition temperature from dynamic scanning at different velocities of the EPO system

As shown in Figure 27 the same specimen was exposed to further cooling and heating ramps, in order to evaluate the presence of crystalline phases and to measure the glass transition temperature (Tg). Final results lead to the conclusion that no crystallization transitions were recorded thus assuring that the formed polymer system is fully amorphous. Glass transition temperatures has been also measured and reported in Figure 28. A wide range of Tg has been measured, from 71°C up to 91°C, by scanning at heating rates from 1 to 10 °C/min. Normally higher heating rates will shift Tg to higher values. In this case variations are more significant, and this could be suitably associated to the heating rates during the first polymerization stage: at lower heating rate the system reacts as fast that vitrification occurs before the arising of the temperature system. Subsequently at lower heating rates the global polymerization efficiency is lower and the total reaction heat is lower. This trend is, also, confirmed by the reaction enthalpy described above, in fact their values monotonically increase by increasing heating rate.

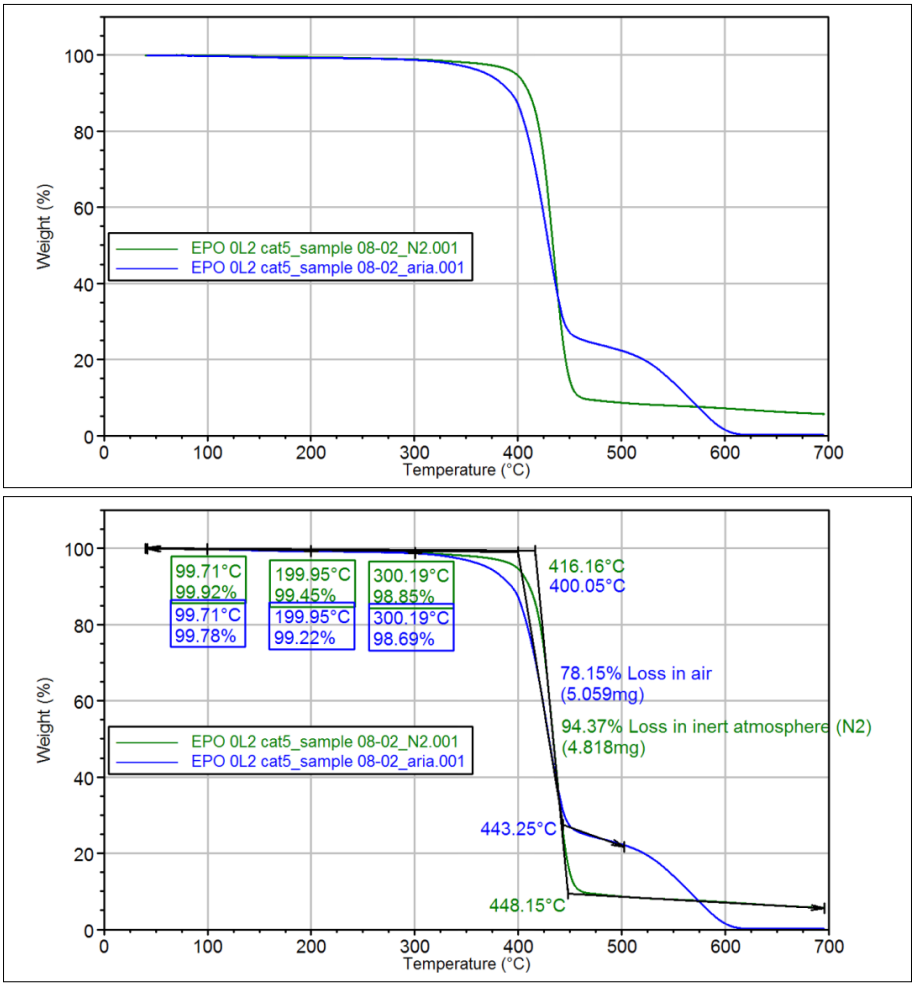


Figure 29 – Thermo-gravimetric analysis (TGA ) of the polymerized EPO system (in Air and Nitrogen)

Thermo-gravimetric analysis (TGA) of the polymerized product confirmed its good thermal stability (up to 300°C. Figure 29 reports the experimental curves for TGA tests conducted in air and nitrogen atmosphere, respectively, in order to compare oxidation and pyrolysis effects. The system behaves quite similarly in oxidative and inert ambient at high temperatures due to the high amount of oxygen atoms in its chains. The most of the degradation takes place near 400°C. The reaction between carbon and oxygen already present in the polymer chains is confirmed by the higher weight loss which occurs in inert atmosphere in the range 450-550°C. On the other hand, in oxidative atmosphere, the fully degradation takes place completely before 600°C. Carbon residues, at 600°C or above are, obviously, not the same due to the persistency of unreacted carbon, in inert atmosphere.

The rheological behaviour of the EPO system has been characterized in the uncured state, during polymerization and after. The whole process has been carried out on the same liquid uncured specimen, by optimizing the test parameters. Using an Anton Paar Physica MCR301 Rheometer it has been possible to set up on the same specimen a first oscillatory test, to investigate the uncured state and the polymerization stage, and a second, subsequent, rotational test, in order to evaluate the viscosity of the polymeric melt. Test parameters were the same used for the test performed to optimise the polymerization. The entire temperature profile is detailed in Figure 30.

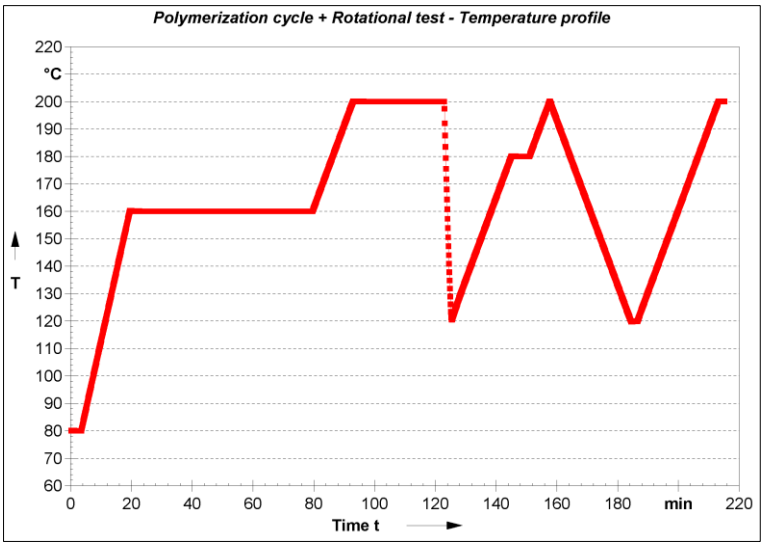


Figure 30 – Temperature profile for rheometric polymerization test, followed by a heating/cooling ramps to the in rotational the final thinness

Results of the oscillatory test are reported in Figure 31**Errore. L'origine riferimento non è stata trovata.**. The same viscosity profile described in the early section has been obtained. In figure are reported also the storage and loss shear moduli, G' and G". The main aspect, which can be highlighted by using these information is that the system never gel during the entire polymerization cycle. The gelation condition is reached when G" became greater than G' and the gel point is identified by the crossing of G' and G" curves.

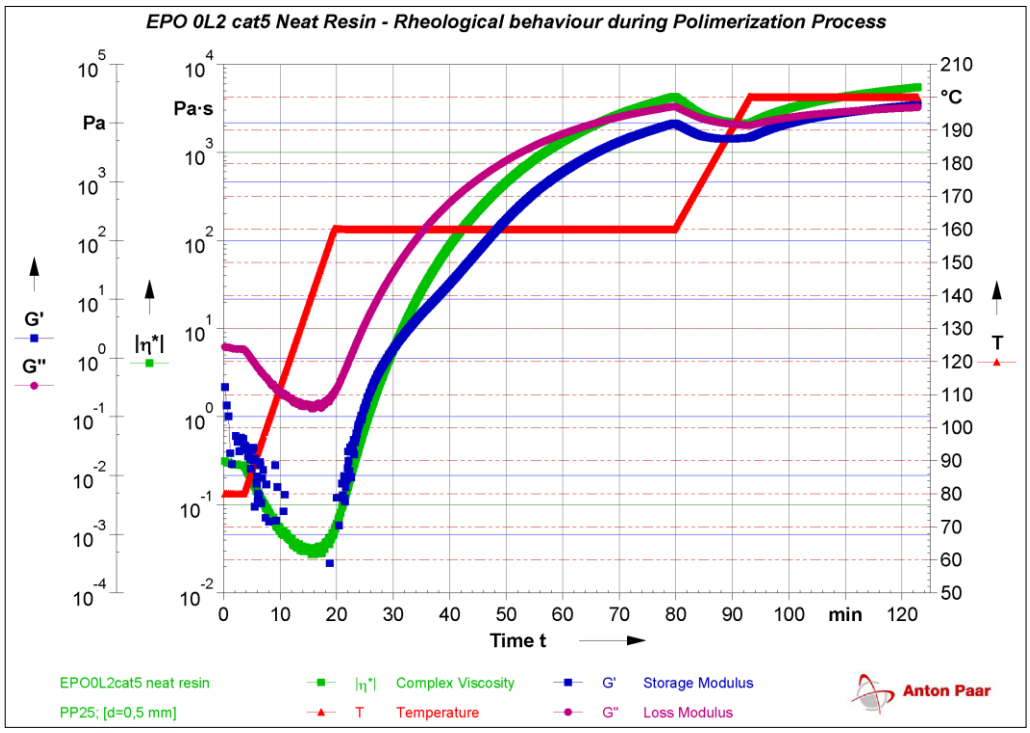


Figure 31 – Rheological behavior of the catalyzed EPO during optimized, two stages, polymerization cycle

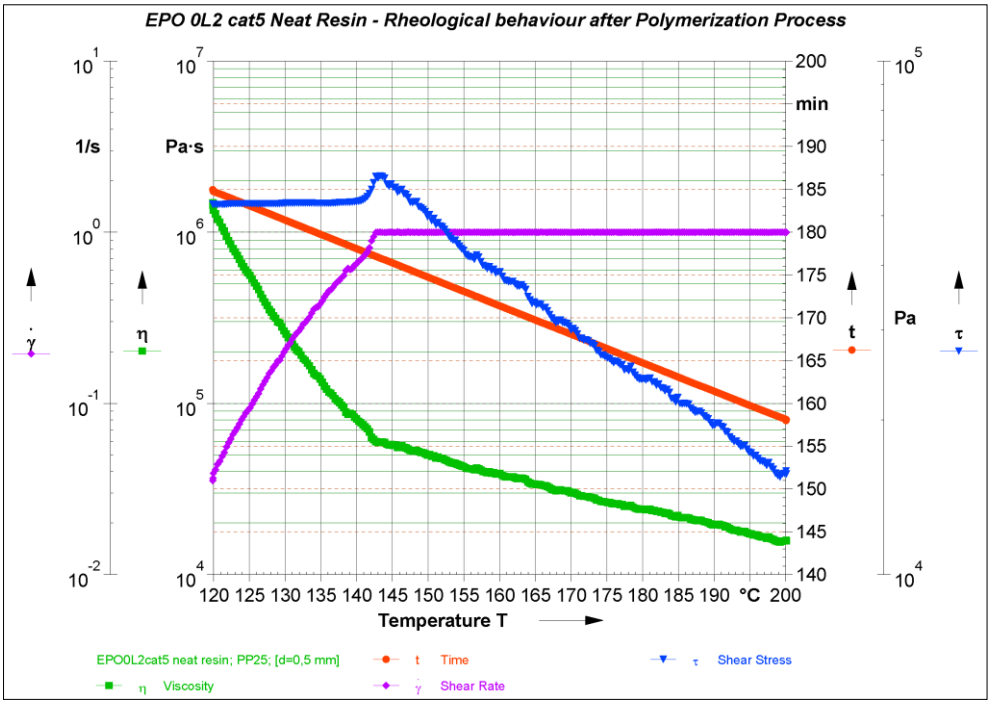


Figure 32 – Rheological behavior of the catalyzed EPO after optimized, two stages, polymerization cycle

In Figure 32, moreover, is reported the rotational test after polymerization. The viscosity was measured at constant shear rate and varying temperature. Near 140°C the applied torque to maintain constant the shear rate became too high for rheometer, than shear rate falls down and the measured viscosity under 140°C is not directly comparable with measures performed over 140°C. In the range 140-200°C the viscosity decrease from 60˙000 to 15˙000 Pa·s.

Dynamic mechanical test (DMA) has been, also, carried out. Rectangular specimens of polymerized material were prepared for single cantilever test configuration and tested by applying a strain of 0.1% in oscillatory mode at 1Hz. A temperature ramp of 3°C/min was set to arise the temperature from -50°C up to 150°C. Results were reported in Figure 33. Main output of DMA test are the storage modulus, the glass transition temperature and the tanδ peak.

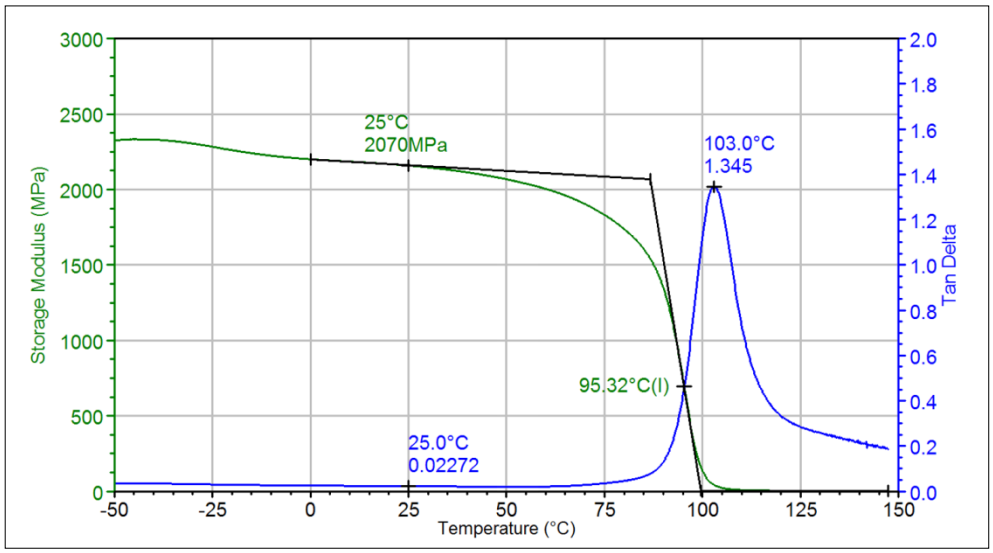


Figure 33 – DMA test of the polymerized bisphenols/DGEBA mixture

The average storage modulus at 25°C was found 2070MPa which corresponds to typical value of an epoxy polymer. The measured glass transition temperature was 95°C; according to the literature, the value is greater than the equivalent measured using DSC test due to finite size of the sample. The tanδ peak was measured at 103°C, its value (1.345) is greater than 1, then the material exhibits a liquid-like

behavior at temperatures higher than Tg . Thermoset epoxy polymers tanδ is always less than 1, due to the cross-linked network, which bring to a solid-like behavior.

Finally, in Table 6 are summarized the characterization data of EPO system, in the uncured state, the polymerization schedule and the main features of the cured polymer.

Table 6 – Properties of thermoplastic epoxy-based reactive system (EPO)

| **Reactive Mixture** | | |
|---|---|---|
| Density (25°C) | $g/cm^3$ | 1.14-1.18 |
| Viscosity | mPa·s | ~250˙000 (25°C)<br>~20˙000(40°C)<br>~250(80°C)<br>~70(100°C) |
| **Polymerization process** | | |
| Activation temperature | °C | >100 |
| Reaction Heat ($\Delta H_{reaction}$) | J/g | 200-250 |
| Polymerization Schedule | warm up: | 80°C<br>hold time: as request |
| | 1st stage: | up to 160°C<br>rate: 5°C/min or higher<br>hold time: 60min (max) |
| | 2nd stage: | up to 200°C<br>rate: 5°C/min or higher<br>hold time: 30min (max) |
| **Polymerized product** | | |
| Density (25°C) | $g/cm^3$ | 1.16-1.18 |
| Molecular arrangement | | 100% amorphous |
| Glass transition Temperature - Tg | °C | 75-90 |
| Thermal stability | °C | >300 |
| T onset start degradation | °C | 400 (in air)<br>415(in nitrogen) |
| Carbon residue after degradation | % | ~12 |
| Bending Modulus (DMA Test) | MPa | 2070 (25°C) |

| | | |
|---|---|---|
| Tan δ peak (DMA Test) | | 1.345@103°C |
| Viscosity (Rotational test) | Pa·s | ~60˙000 (140°C)<br>~15˙000 (200°C) |

## 3.6 References


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# PART B
# NANOCOMPOSITES AND FIBRE REINFORCED COMPOSITES

# 4.

# POLYMER NANOCOMPOSITES

## 4.1 Summary

In this chapter polymer nanocomposites are introduced, in particular epoxy/carbon nanotubes composites. Various approaches to improve the dispersion, orientation, and adhesion of CNTs are reviewed.

The core of this part is represented by nanocomposites manufacturing made by thermoplastic epoxy-based reactive system formerly developed.

The aim is to join all advances in nanocomposite manufacturing developed for thermosetting polymers and the properties of thermoplastic polymers. Several examples of thermoplastic based nanocomposites are present in literature, most of them produced using hot melt processing. Here thermoplastic nanocomposites have been produced by reactive processing, which has been until now, perquisite of thermosetting matrices. The resulting nanocomposite properties are described in the following paragraphs.

## 4.2 Epoxy/Carbon nanotubes Nanocomposites

Polymer nano-composite matrix could be the ideal solution for a new generation of composite materials. The continuous demand for new high performance polymer composite for various applications, in different industrial sectors, has lead many

researchers to investigate the potential use of carbon nanotubes (CNTs) as nano-reinforcements of polymer matrix for the manufacturing of traditional laminate composite[1].

Carbon nanotubes (CNTs), both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have attracted a great deal of interest, since they were first described in the early 1990s. Because of their superior tensile modulus, strength, electrical conductivity ($>10^4$ $S \cdot cm^{-1}$), and thermal conductivity (>200 $W \cdot m^{-1} \cdot K^{-1}$), as well as large aspect ratio, CNTs have become ideal candidates for use in multifunctional polymer composite applications. The first polymer nanocomposite using CNTs as a filler was reported in 1994 by Ajayan et al.[2].

CNTs have attracted considerable attention due to their unique mechanical, surface, multifunctional properties and strong interactions with the hosting matrix mainly associated to their nano-scale features. CNTs' impressive mechanical properties, with stiffness and strength values falling within the range of 100-1000 GPa and 2.5-3.5 GPa, respectively, make them ideal candidates to develop novel composites characterized by advanced polymer matrices[3].

Despite the enormous amount of experimental data available in literature[4,5], there are still controversial results concerning elastic property, strength and fracture toughness; moreover, due to inherent difficulties in processing these unconventional nanostructure as nano-fillers in polymer system, a reliable theoretical correlation of the experimental data is still in shadow[1].

Since then, CNTs have been extensively studied in a wide range of polymer matrices for composite applications[6,7,48]. Considering that the characteristic dimensions, especially diameter, of the CNTs are on the same scale as the polymer chains, CNTs are expected to reinforce the hosting matrix material on molecular scale. This matrix/filler interaction should greatly enhance the physical and mechanical properties of the final material as a whole. Compared to SWCNTs, MWCNTs have the advantages of being lower in cost and easier to disperse,

making them ideal for large-scale polymer nanocomposites production. Hence, MWCNT/polymer composites show great potential for high performance engineering applications.

Epoxy resins are an important class of polymers due to their strong adhesion and excellent overall mechanical properties, including high strength and stiffness, high chemical, thermal and dimensional stability, good creep and solvent resistance. These remarkable performance characteristics, together with their good processability and reasonable cost, have enabled epoxy resins to be used in a wide range of engineering applications. In particular, epoxy-based composites have been extensively used as structural materials in aerospace, military and sporting goods fields owing to their excellent performance. Incorporation of CNTs into epoxy is expected to further enhance the already high performance of epoxy and epoxy composites, and also to bring additional functionalities, such as electrical and thermal conductivity, for applications where low weight, high strength and high conductivity are of primary concern[9].

In the past two decades, the incessant improvements in CNT synthesis, performance and price competitiveness, have made CNTs attractive for various commercial applications. Numerous techniques for preparing epoxy/CNT nanocomposites have been developed. However, huge challenges still exist to fully impart the high strength and conductivity of CNTs to epoxy because most of the final composites properties depend on the dispersion state, adhesion and orientation of tubes within the matrix. Because of the intrinsic van der Waals force attraction, high surface area and high aspect ratio, CNTs are usually present in the form of bundles and ropes. Thus, dispersion of CNTs in a medium, especially in a high viscosity epoxy medium, becomes a challenge. The poor dispersion of CNTs not only dramatically reduces their reinforcing efficiency, caused by the CNTs sliding by each other when forces are applied, but also results in the formation of micro–voids in the nanocomposites. Furthermore, the improvement of CNT dispersion in an epoxy matrix is typically accompanied by an increase in system viscosity, leading to processing difficulties and which, in turn, might negatively

affect subsequent dispersion, orientation and integration processes necessary to prepare multi-functional epoxy nanocomposites. Because of their high aspect ratio and twisting characteristics, CNTs dispersed in a media are usually entangled with each other. This entanglement usually lowers their reinforcing efficiency and prevents subsequent dispersion of CNTs, often resulting in an impairment of electrical and thermal properties of the final composites. Thus, the control of the dispersion state of CNTs in the epoxy matrix is highly desirable.

Poor adhesion between CNTs and epoxy is frequently observed and results from the atomically smooth non-reactive surface characteristics of CNTs. The lack of interfacial bonding limits the load transfer from matrix to CNTs. Poorly adhered CNTs are typically pulled out of the matrix upon failure, thus limiting their reinforcement efficiency.

A great effort has been paid to address the challenges mentioned above, and important progresses have been made. It should be noted that the quality of CNTs utilized, such as purity and chirality, also has a significant effect on the subsequent CNT treatment and nanocomposite preparation. For instance, CNTs grown via chemical vapor deposition ( CVD ) are usually well aligned and, therefore, easier to disperse. Various approaches to improve the dispersion, orientation, and adhesion of CNTs are reviewed in this chapter.

The core of this work is represented by nanocomposites manufacturing produced using the thermoplastic epoxy-based reactive system formerly developed. The aim is to exploit the advantages of a simple manufacturing production technique characteristic of an epoxy system for producing nanocomposites possessing thermoplastic properties.

### *4.2.1 Processing Techniques*

Sonication is maybe the most common dispersion technique for CNTs[10]. It is commonly accepted that sonication waves promote the break-up of large bundles and " peel off " individual CNTs located at the outer layer of the bundles, which

results in gradual dispersion of the CNTs[9] . High intensity and long duration sonication treatment can lead to localized damage and shortening of the CNTs[11,12] that would lead to deterioration of the mechanical, electrical and thermal properties of the CNTs. Sonication has also been frequently used jointly with other treatments for promoting CNT dispersion, such as covalent and non-covalent functionalization, which will be described in the following. In general, mechanical dispersion of CNTs in an epoxy matrix is more difficult than in thermoplastics, mainly because of the relatively low shear forces that are exerted on the epoxy-based systems to achieve dispersion. During regular mechanical or magnetic stirring processes, the shear forces are typically not adequate to effectively disperse the CNTs in the epoxy reactive mixture. Attempts to intentionally enhance the system viscosity in order to increase shear force by lowering temperature have been reported[13]. On the other hand, the system viscosity is often lowered by heating or adding solvents, in order to promote the distribution of the partially dispersed CNT bundles[14]. Typical high shear processing techniques widely used in thermoplastics processing, such as twin-screw extrusion, are rarely used for epoxies. Moniruzzaman et al.[15] mixed epoxy and SWCNTs in a laboratory scale twin-screw mixer and then mixed the compound with a hardener. However, the process scale up remains a challenge. Potential curing during mixing, as well as cleaning and prevention of cross-contamination, are among the issues to be addressed. A calendering technique, which utilizes adjacent cylinders rotating at different velocities to impart high shear stresses, has been adopted by several groups to address the dispersion of CNTs in epoxy[16]. Both the gap between the rolls and the angular velocities are variable, allowing the application of various shear intensities. The strong shear from this approach gives rise to a high degree of CNT dispersion in the epoxy matrix. This approach represents a significant advance toward development of solvent -free, scalable manufacturing processes[16] .

The processing techniques described above significantly improve the dispersion of CNTs in the epoxy, on the other hand, they usually have little impact on the adhesion between CNTs and the epoxy matrix. Thus, surface treatment of CNTs is

still essential, especially for structural applications where mechanical properties are of primary concern.

### *4.2.2 Non-Covalent Functionalization*

Functionalization of CNTs is important both for dispersion and for adhesion needs. Techniques regarding both non-covalent and covalent functionalization of CNTs have been extensively explored[8]. Non-covalent functionalization is mainly based on van der Waals forces and is controlled by thermodynamic criteria. To stabilize the dispersion, other molecules are used to prevent the re-aggregation of CNTs by creating electrostatic repulsions and/or steric barrier between CNTs. The attached molecules may also modify the surface properties of the CNTs, making them more compatible with some solvents and epoxy monomers. One major advantage of non-covalent functionalization is that this approach can effectively improve CNT dispersion without damaging the CNTs; thus there is no tube property degradation[8]. Although the non-covalently attached molecules might help for a better interface between the CNTs and the epoxy, potentially improving the adhesion between the CNT and the surrounding epoxy matrix, the lack of chemical bonding at the interface usually does not allow for effective load transfer. As a result, the improvement in mechanical properties is typically limited[15,8].

One of the most typical methods of non-covalent functionalization is based on amphiphilic molecules such as surfactants. Usually, the hydrophobic part of the amphiphilic molecules interacts with the CNT surface, while the hydrophilic part brings to electrostatic repulsions between CNTs encouraging the dispersion stability.

### *4.2.3 Covalent Functionalization*

Compared to non-covalent functionalization, covalent functionalization not only improves the dispersion of CNTs, but can also potentially introduce the possibility of chemical bonding between functionalized CNTs and an epoxy matrix, thus making it particularly suitable for load -bearing structural applications.

To maximize the interaction between CNTs and epoxy, the functionalized CNTs are usually designed to serve as cross-linkers for the thermoset epoxy, which allows them to be integrated into the epoxy network[17]. According to molecular simulation[18], the shear strength of a polymer/CNT interface can be improved by over one order of magnitude with the introduction of a low density of chemical bonds ( < 1% of CNT carbon atoms) between the CNT surface and the polymer matrix. On the other hand, the functionalization of CNT surfaces introduces extreme physical and chemical conditions that usually result in defects on CNT surfaces. These defects lead to weakening in the mechanical, electrical, and thermal properties of CNTs. Considering the extremely high strength of CNTs, such a minor reduction in mechanical strength should not affect the overall reinforcement effect of CNTs in polymers. However, the deterioration in electrical properties (and probably thermal properties as well) might be more profound because each covalent functionalization site scatters electrons[6] .

Most of the CNT functionalization processes are carried out by surface pre-treating by oxidation, including strong acid oxidization, ozone oxidation, plasma oxidation, and fluorination. Strong acid oxidization is the most frequently used oxidation approach for CNTs, usually involving sulphuric acid, nitric acid, or their mixture. Sometimes, hydrogen peroxide is also added to assist the oxidation reaction. The oxidized CNTs from the above approach typically contain carboxylic acid groups ( – COOH), carbonyl groups (– CO– ), and hydroxyl groups ( – OH) on their side wall surfaces and end caps[19]. Oxidized CNTs can be further treated with hydrochloric acid to promote the formation of carboxylic acid groups (converting carboxylate groups to carboxylic acid groups)[20]. Oxidized CNTs have better solubility and can form well - dispersed electrostatically stabilized colloids in water and organic solvents. When the oxidized CNTs are directly used for epoxy/ CNT nanocomposite preparation, improvement in mechanical and thermal properties is already evident, which can be mainly attributed to their improved dispersion.

The functional groups on the oxidized CNT surfaces, primarily the carboxylic acid groups, provide a large versatility due to their versatile chemistry. Further chemical

modifications can be carried out, by achieving better adhesion between the CNTs and the epoxy molecule. Either the carboxylic acid groups or the further derivate functional groups can react with either the epoxy monomer or the curing agents. Owing to the multi-functionality on the CNT surfaces, cross-linking of CNT with the epoxy network is also possible. The carboxylic acid groups on CNT surfaces can directly interact with epoxy resin via a ring opening reaction, and can participate in the subsequent curing reaction, thus integrating the CNTs into the epoxy network. This reaction should be performed before adding curing agent, which might also react with carboxylic acid groups on the CNT surfaces. Another widely adopted derivate of carboxylated CNTs is to interact with amines. Because amines are typical curing agents for epoxy, the unreacted amino groups can be co-cured with epoxy resin, integrating the CNTs into the epoxy network.

Fluorination of CNTs and the subsequent derivate provide another versatile tool for the functionalization of CNTs for nanocomposite applications. The fluorination of CNTs significantly enhances their chemical reactivity and solubility while maintaining their mechanical properties and thermal conductivity because no carbon atoms are displaced and the tube structure remains defect–free. Fluorinated CNTs are soluble in alcohols and other polar solvents . Thus, they can be directly mixed with epoxy monomer and curing agent for the preparation of epoxy/CNT nanocomposites, and have been reported to be very effective in reinforcement of epoxy[21].

### *4.2.4 Effect of CNT on the Curing of Epoxy*

In the majority of the literature, the authors typically adopted the same formulations and procedures to cure epoxy/CNT samples as with the neat epoxy systems. The comparison is based on the assumption that the addition of CNT will have little or no effect on the curing of epoxy, including the curing reaction stoichiometry and curing reaction kinetics. Unfortunately, this is not the case for most of epoxy/CNT systems. The surface functionalized CNTs, especially those that are intended to be integrated into an epoxy network, are usually expected to be involved in the curing reaction. In some cases, after the functionalization of the CNTs the excessive

functionalization agent is left in the epoxy system, potentially interfering with the intended curing reaction. Even pristine CNTs can potentially affect the curing kinetics by altering the physical properties of the epoxy, such as thermal conductivity[9].

In general, the effect of CNTs on the curing reaction of epoxy can be considered into two main cases. In the first case CNTs themselves are not involved in curing reactions, but they change the physical properties of the epoxy, especially rheological behaviour of the reactive mixtures, then the curing kinetics is altered. In the second case the functional groups on the surface of CNTs are involved in the curing reaction. In some cases, functionalized CNTs may have multiple effects on epoxy curing. Various degrees of CNT functionalization and CNT concentrations may also influence curing reactions to a different degree or sometimes with opposite effect, which might account for some inconsistent findings reported in the literature.

Pristine CNTs have been reported to accelerate the epoxy curing reaction[22], as evidenced by higher initial reaction rates, lower initial reaction temperatures, and a shift of the exothermic reaction peak to lower temperatures during isothermal DSC characterization. By increasing concentrations of CNTs, the time to the maximum reaction rate is decreased. Such an acceleration effect is caused either by the extremely high thermal conductivity of CNTs or by a low concentration of hydroxyl groups on the CNT surface created during the CNT purification process, which may catalyze epoxy ring opening in the initial stage of reaction. It has, also, been found that the addition of CNTs into epoxy decreases the overall degree of cure compared to neat epoxy under the same curing conditions, which is possibly due to the steric hindrance of CNTs impacting the mobility of the monomers and curing agent. As a result, the glass transition temperature (Tg) of the epoxy/pristine CNT nanocomposite is usually lower than neat epoxy according to some reports[23].

Most of the covalent functionalization of CNTs starts from their oxidation, which helps in forming carboxylic acid and hydroxyl groups on the CNT surfaces[19]. The potential effect from hydroxyl groups has been discussed above[22].

Amine functionalized CNTs, because the amine molecules on the CNT surfaces can serve as curing agent, the curing reaction stoichiometry is altered, leaving excess curing agent.

Fluorinated CNTs have also been reported to affect the curing reaction stoichiometry and process[21] . Fluorinated CNTs can react with amino groups of the amine curing agents, thus altering the curing reaction stoichiometry. Another side reaction involves the fluorine atoms on the fluorinated CNT surface, which become free radicals at high temperatures and attack epoxide rings .

This results in a non-stoichiometric formulations if the curing agent amount is not correctly tuned, a lowering of the cross-linking density of the epoxy network occurs, as evidenced by a lower Tg and lower decomposition temperature. The mechanical properties of epoxy/CNT, such as storage modulus, are also affected due to the altered curing reaction[21].

As discussed above, the direct or indirect effects of CNTs on the curing reaction can lead to important thermal and mechanical property changes of epoxy/CNT nanocomposites, which would make difficult their property evaluation.

### *4.2.5 Alignment of CNTs in Nanocomposites*

After CNTs have been well dispersed in an epoxy matrix, in order to further optimize the performance of the epoxy/CNT nanocomposites, a preferred orientation or network of the CNTs in the epoxy matrix can be achieved. It should be noted that, if CNT dispersion is excessively good, the formation of a CNT network with established conductive pathways can be prevented. In such cases, a certain level of controlled aggregation is desired.

A number of approaches have been developed to align CNTs. The chemical vapour deposition (CVD) approach produces well aligned CNTs during synthesis. More commonly, CNTs are aligned when suspended in media under magnetic or electric fields[24]. Well-aligned arrays of CNTs generally tend to randomize and form clusters upon mixing in an epoxy matrix. The high viscosity of the epoxy usually

complicates the alignment process. Thus, new approaches need to be developed by either directly aligning CNTs in a viscous epoxy or impregnating the epoxy with pre-aligned CNTs, or by other novel routes. Epoxy composites that contain oriented CNTs are expected to offer considerable advantages over those containing random dispersion of bundled tubes[25].

### *4.2.6 Electrical Properties of thermoset Epoxy/CNT nanocomposites*

The key to achieve a low percolation threshold and high conductivity in epoxy is to induce a conductive CNT network while minimizing the aggregation of CNTs. Some processing parameters that could promote the dispersion of CNTs, such as stirring power, duration of stirring, and resin viscosity, might lead to the destruction of the CNT network in an epoxy matrix. Any processing parameters that can facilitate the CNT network formation should be considered and manipulated[26]. For example, it has been recognized that a relatively high curing temperature is advantageous for CNT network formation by enhancing the mobility of the CNTs[26]. Various strategies for aligning CNT or forming a CNT network in an epoxy matrix have been developed, some of which were discussed earlier. The conductive epoxy/CNT nanocomposites are expected to supply various applications, such as anti-static[14], electromagnetic interference (EMI) shielding[27], and field emission source, depending on their magnitude of conductivity.

It should be noted that the functionalization approaches for improving CNT dispersion usually lower the electrical conductivity percolation threshold because of the improved dispersion. However, the molecules on the CNT surface (either covalently or non-covalently bonded) exhibit lower bulk conductivity. Without any surface functionalization, CNTs in the composites are still typically separated by a thin layer of polymer matrix material. The thin functionalization agent layers or polymer layers operate as a barrier to the electrical charge transfer between nanotubes[28]. Related simulation studies have calculated that the tunnelling distance due to the insulating film between adjacent CNTs in polymer/CNT composites is about 1.8 nm and indicated that the contact resistance and tube-to-tube distance

play a dominant role in the electrical conductivity of polymer/CNT nanocomposites[28] .

Windle and coworkers[14,26,29] carried out methodical research in this field and set records for achieving the lowest percolation threshold values for conductivity. They reported a low percolation threshold of < 0.04 wt% in epoxy by using entangled pristine MWCNT produced by decomposition of hydrocarbon gases, even though MWCNT aggregates were still formed[14]. Later, a much lower percolation threshold of about 0.0025 wt% and a bulk conductivity of $10^{-3}$ $S \cdot m^{-1}$ at 0.005 wt% were achieved using straight and un-entangled pristine MWCNTs produced by a CVD process[14]. They further reduced the percolation threshold to 0.0021 wt% by using shorter CVD grown MWCNTs[26]. The low percolation threshold and high conductivity are mainly due to the CVD grown MWCNTs, which are much less entangled compared to the CNTs from other synthesis techniques.

The electrical behaviour created from CNT dispersion and formation of a CNT network can also be used to evaluate the CNT dispersion level. Hsu et al.[30] developed a method to characterize the degree of CNT dispersion in a polymer matrix based on AC impedance spectra. Their results have shown that the composite film capacitance is a more accurate indicator than film resistance for evaluating nanotubes dispersion.

### *4.2.7 Mechanical Properties of thermoset Epoxy/CNT nanocomposites*

A large variety of polymer/CNT nanocomposites have been studied in the past decade [4, 7, 8, 22, 31]. In general, the results have shown that CNTs can more effectively reinforce thermoplastics than thermosets, possibly because the dispersion of CNTs in thermoplastics is generally more readily accomplished where shear mixing, stepwise dispersion, and elongational flow mixing are more effective. Another potential reason for the limited reinforcement effect of CNTs in epoxy is the lower thermal expansion coefficient of the cured epoxy. The low shrinkage upon cooling to room temperature inevitably compromises the load transfer, especially if strong bonding between the CNTs and the epoxy matrix is not established. This

hypothesis can be indirectly supported by the fact that load transfer in epoxy/CNT nanocomposites is significantly better in compression than in tension[32]. It should be noted that , although it has been widely accepted that theoretically a higher aspect ratio of CNTs should be more beneficial for reinforcing epoxy, it is not necessarily the case in practice[33], due to more difficulties in dispersion alignment of high aspect ratio CNTs.

In one of the first reports on epoxy/CNT nanocomposites, Schadler et al.[32] achieved about 20% Young ' s modulus increase (from 3.1 to 3.71 GPa) by using 5 wt% of pristine MWCNT. By using 1 wt% HiPco SWCNTs with both open-end oxidation and sidewall fluorination, Zhu et al. reported a 30% increase in Young

modulus (from 2.0 to 2.6 GPa) and an 18% increase in tensile strength (from 83.2 to 95.0 MPa)[34]. This significant improvement was attributed to the homogeneous dispersion of fluorinated SWCNTs in the epoxy matrix, which was undetectable under TEM. Much higher mechanical property improvements were reported in ductile, rubbery epoxy matrices that were incompletely cured [35, 36]. For example, Allaoui et al.[37]doubled the Young's modulus of neat epoxy from 0.118 to 0.236 GPa with 1 wt% pristine CVD grown CNTs. At a loading of 4 wt% pristine CNT, the Young ' s modulus of the epoxy/CNT nanocomposite was further increased to 0.465 GPa, which is approximately three times higher than that of neat epoxy. When the stiffness of the epoxy matrix is formerly high, the contribution of CNTs is limited, due to the poor load transfer between the two components.

However, with low stiffness epoxy matrices, a substantial portion of load can be transferred to CNTs through interfacial interaction, leading to a more significant stiffness improvement.

By infusing epoxy into as - grown arrays of vertically aligned CNTs, as described above, Wardle and coworkers improved the Young ' s modulus by about 220%, compared to the neat epoxy, at a loading of 2 vol% of unmodifi ed CNT[38] . Wang et al.[39] managed to incorporate up to 39 wt% of SWCNT in epoxy via a similar resin infusing approach based on pre - formed CNT films. DMA results showed that the

storage modulus of the resulting nanocomposites could reach as high as 15 GPa, more than four times higher than that of neat epoxy.

It has also been reported that the incorporation of CNTs into epoxy can enhance the fracture toughness of the epoxy[40, 41], possibly because of the bridging effect during loading. However, formation of voids because of either incomplete degassing or CNT aggregation easily offsets the observed improvements[40]. Overall, the literature results have clearly shown that both functionalization and orientation are effective tools to improve the mechanical properties of epoxy/CNT nanocomposites. However, the mechanical property improvement achieved so far is still well below the theoretical calculation and expectation. For these reasons, interest in the further improvement of stiffness and strength of epoxy/CNT nanocomposites for structural applications still remains an up-to-date subject for the scientific community.

Different approaches to build an appropriate theory for predicting reinforcement efficiency of CNTs within a hosting matrix have been presented in the literature. Indeed, the reinforcement capability of carbon nanotubes in a polymeric matrix will depend on their amount, but, undoubtedly, their arrangement within the hosting medium plays also a fundamental role in the load transfer mechanism. For this reason, the state and level of dispersion need to be accounted in any attempt for predicting the mechanical behaviour of the final nano-composite system. In literature the enhancing reinforcement of CNT loading for the Young's modulus is commonly reported. However, at the same time, discrepancy among the different data is highlighted. Therefore, an important issue for modelling purpose is the lack of a reliable database for this property. Characterization and structure-properties of nano-mechanics modelling research have shown that enhancement in mechanical properties of nano-composites are strongly dependent upon the level of dispersion and the final morphology of the nano-fillers. CNTs dispersion process still represents a critical issue to allow the potential usage of these nanostructure as reinforcements. Dispersion and homogenization stands as a very complex

phenomenon due to the natural tendency of CNTs to bundle and to aggregate mainly due to Van der Walls interactions among nanotubes[10, 1].

From the theoretical point of view, different parameters could be considered to quantify the reinforcement effect of nano-filler within the final nano-composite system. Based on classical Cox's approach, developed for paper and other fibrous materials to analyse the effect of orientation of the fibres on the stiffness and strength, a suitable expression for the effective reinforcement modulus of paper and fibrous materials can be defined as follows[1]:

$$E_h = \frac{(E_C - E_m)}{V_{filler}} + E_m \qquad (1)$$

where $E_C$ and $E_m$ represent, respectively, the modulus for the final composite and the hosting matrix and $V_{filler}$ is the nanotubes volume fraction. Previous equation represents the equivalent modulus of reinforcement according to the measured value of the final nano-composite.

Figure 34 reports the reinforcement efficiency, computed on literature data, taken from different research works.

The data reported, in Figure 34, are related with lowest nanotubes content (dilute regime) which should correspond to the minimum level of nanotubes clustering and thus highest level of dispersion for each set of data. Since the nanotubes modulus values range from 1000 GPa to 3000 GPa according to Treacy et al.[3]., the enhancement of elastic modulus showed by the reported data appears extremely low with a remarkable spread.

Analysis of the data reported in Figure 34 reveals that the obtained efficiency of reinforcement is sensibly lower than expected, supporting great efforts to develop more standardised manufacturing processes and, hence, to gather more reliable data.

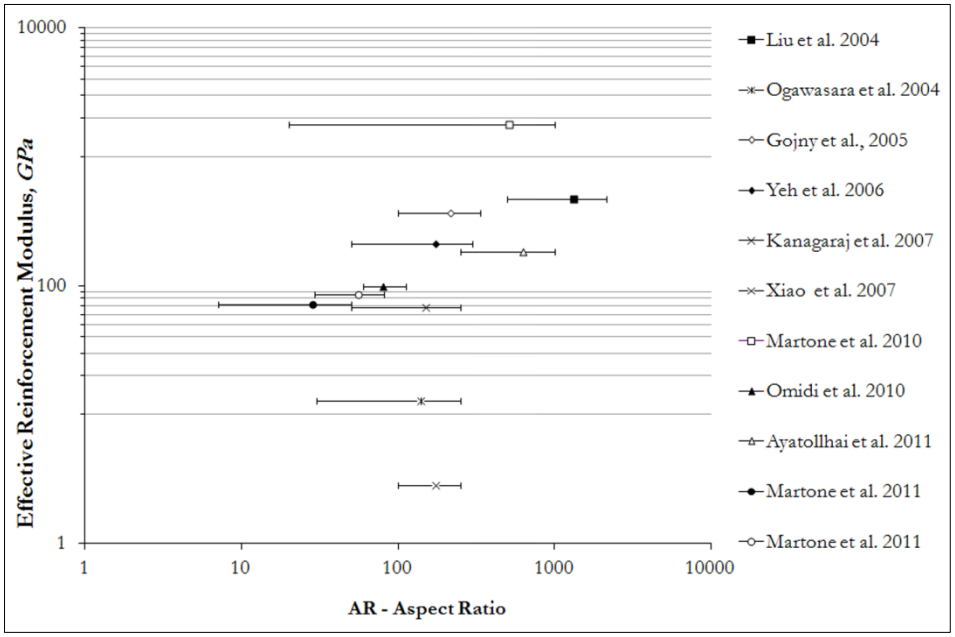


Figure 34 - Effective reinforcement modulus as function of nanotubes aspect ratio, by Martone et al.[1]

## 4.3 Preparation of Thermoplastic Epoxy/ CNT Nanocomposites

A high degree of dispersion of the CNTs in the epoxy matrix is usually a prerequisite CNT/epoxy nanocomposite preparation. Many strategies, covering both processing techniques and CNT modifications, have been developed. In many cases, multiple treatments are combined to achieve an optimal result.

In terms of process techniques, the mechanical mixing via calendaring gives rise to high shear forces with a consequent high degree of CNT dispersion in the epoxy matrix. An alternative to three roll milling, which, anyway, ensure a mixing by shear forces is represented by homogenizers with rotor-stator configurations. This kind of tool represents the best choice to achieve the industrial process scale-up, for the reason that technology supply by now homogenizers of every size and optimized for each filler that has to be processed. As represented in Figure 35, due to the high rotation speed of the rotor, the medium to be processed is drawn axially into the dispersion head and then forced radially through the slots in the rotor/stator arrangement. The high accelerations acting on the material produce extremely

strong shear forces, that, together with the turbulence occurring between rotor and stator, assure a homogenous dispersion.

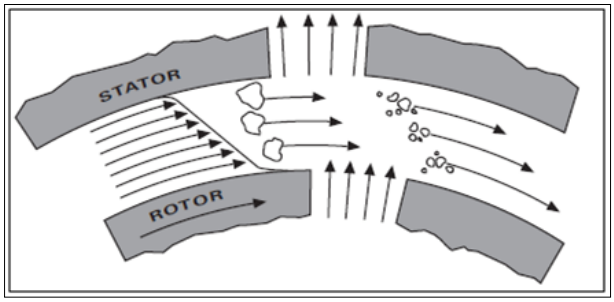


Figure 35 – Fluxes generated by batch mixer dispersion head

The processing techniques described above significantly improve the dispersion of CNTs in the epoxy, on the other hand, they usually have little impact on the adhesion between CNTs and the epoxy matrix. Thus, surface treatment of CNTs is still essential, especially for structural applications where mechanical properties are of primary concern.

In this experimental work, three different kinds of nanocomposites have been produced using the new formulated thermoplastic epoxy-based reactive system and three different types of nanotubes. Nanocomposites containing untreated MWCNTs, without any functionalization, together with composites containing two different types of functionalized nanotubes have been produced at by various nanotubes concentration. The functionalization has been selected by considering the chemical compatibility with our reactive system. In our resin formulation co-curing agents are bisphenols, then more compatible functionalization are hydroxyl and carboxyl. Since OH-MWCNT has the same functionalization of co-reactive curing agent, surely is fully compatible, both in terms of solubility and in terms of reactivity with epoxy. Then the polymerization scheme is slightly altered. With COOH-MWCNT a better solubility can be predicted, but the polymerization scheme is altered, because they behave as carboxylic acids and, during polymerization, the production of water as by-product is expected.

### *4.3.1 Materials*

The thermoplastic epoxy-based system used has been well described in previous chapters. The addition of nanotubes in the reactive mixture has been neglected in terms of stoichiometric unbalance, therefore no correction has been done. In the following, the neat basic system will be labeled, sake of simplicity, briefly "EPO".

Three types of nanotubes have been used in this work for producing three different types of composites. Catalytic carbon vapor deposition (CCVD) grown MWCNTs NC 7000, with an average diameter of 9.5 nm, an average length of 1.5 μm and a purity of 90% were purchased by Nanocyl S.A.; COOH-MWCNT, NC 3151, with an average diameter of 9.5 nm, a length of less than 1 μm, a purity exceeding 95% and a carboxylic functionalization of about 4 % were purchased by Nanocyl S.A.; OH-MWCNT, TN-MH3 with a diameter between 10 and 20 nm, a length between 10 and 30 μm, a purity exceeding 95% were purchased by Chengdu Organic Chemicals Co.o Ltd., Chinese Academy of Sciences (see also Table 7).

All nanotubes have been used as received without any extra purification treatment. Since moisture can alter the polymerization stage of epoxy reactive system, nanotubes have been dried at 110°C for 6h at 10kPa absolute pressure.

Table 7- MWCNTs Properties

| **Description** | **Outer Diameter (nm)** | **Length (μm)** | **Density ($g/cm^3$)** | **Purity (%)** | **Functionalization Content** |
|---|---|---|---|---|---|
| *NANOCYL NC7000* | 9.5 | 0.5-10 | 1.55 | >95 | - |
| *TIMESNANO TNMH3* | 10-20 | 10-30 | 2.10 | >95 | -OH (3.06 %wt) |
| *NANOCYL NC3151* | 9.5 | 1 | - | >95 | -COOH (4 %wt) |

### *4.3.2 Manufacturing*

MWCNT/epoxy suspensions have been produced using a IKA Ultra-Turrax T25 batch mixer. The entire mixing process has been performed under 100°C, to prevent resin pre-polymerization

Nanotubes have been dispersed in the resin for one hour at different concentrations ranging from 0.005 to 5 wt% depending on the type of nanotubes. In order to improve shear efficiency in dispersing the temperature was set up to 80°C. At this temperature the reactive mixture exhibits a viscosity near 250mPa·s. To avoid unwanted overheating phenomena, the temperature has been also monitored directly inside the resin during the dispersion process and a maximum temperature of 90 °C has been measured after 15 minutes of mixing.

After the dispersion, the catalytic paste (alchidic salt pre-homogenized in liquid DGEBA in concentration of 15%wt) has been added to the MWCNT suspension in the quantity of 5 wt% and the components have been mixed using a planetary centrifugal vacuum mixer for 5 minutes, contemporary providing a homogenous mixing and the degassing of the solution by rotation and revolution movements under vacuum pressure reduction. First attempts of mixing catalyst and resin by hands resulted in very porous composites containing many bubbles.

The fast increase of viscosity, characteristic of EPO system, didn't allow to degas for long time at room temperature, moreover long degassing processes at high temperature have been avoided for not modifying nanotubes dispersion , which is very sensitive to temperature changes.

Once mixed the components, the suspensions have been cured according to optimized polymerization cycle described in chapter 3, and reported in Table 6.

All the composites with the different types of nanotubes have been produced using the same procedure described above. Composites containing NC 7000 nanotubes have been, coded as *n*-EPO, the ones containing carboxylic functionalized nanotubes as *c*-EPO and the ones containing hydroxyl functionalized nanotubes as

*h*-EPO (see Table 8). In the following these codes will be used to refer to the group of composites.

Table 8 – Nanocomposites manufactured

| Nanocomposites group | Functionalization Type | Final NT Content %wt |
|---|---|---|
| *n-EPO* | - | 0.005 |
| | | 0.010 |
| | | 0.020 |
| | | 0.048 |
| | | 0.096 |
| | | 0.190 |
| *h-EPO* | -OH | 0.009 |
| | | 0.099 |
| | | 0.191 |
| | | 0.478 |
| | | 0.942 |
| *c-EPO* | -COOH | 0.465 |
| | | 0.941 |
| | | 4.750 |

## 4.4 Properties of Thermoplastic Epoxy/ CNT Nanocomposites

While the initial intention to incorporate CNTs into epoxy was mainly to enhance the mechanical properties for structural applications, additional functionalities of CNT/epoxy nanocomposites have been identified and achieved. A great disparity in experimental findings has been seen in the literature, owing to the large variations in the characteristics of CNTs from different sources, choices of different epoxy formulations, and different functionalization and preparation techniques. Thus, direct comparisons of the physical and mechanical properties of epoxy/CNT nanocomposites from different reports will not be made here.

### *4.4.1 Electrical Properties and morphology of n-EPO composites*

Circular samples of 40 mm diameter, with a thickness of about 1 mm have been polished and round-shaped pads 15 mm have been painted on the flat surfaces with silver conductive paint. Bulk electrical resistance has been evaluated by means of direct current (DC) measurements through the thickness of the sample, using a picoammeter connected to a two-probes station (Signatone 1160 probe station) at a constant applied voltage of 1 V.

Optical microscopy analysis was carried out on 500 μm thick samples in light transmission mode using an Olympus BX51 microscope.

Figure 36 shows the percolation curve of the n-composites, such as the dependence of the electrical conductivity on NC 7000 content. The electrical conductivity of n-composites increases as the weight percentage of NC 7000 increases. A step enhancement of four orders of magnitude in conductivity can be appreciated passing from 0.0047 to 0.0095 NC 7000 wt%. According to the percolation theory, the percolation threshold value, $wt_c$, can be calculated by equation (2).

$$\sigma \propto (wt - wt_c)^t \qquad (2)$$

for $wt > wt_c$, where σ is the electrical conductivity, wt is the weight percentage of conductive fillers and t is the critical exponent of conductivity. The inset in Figure 36 reports the plot of logσ vs log(wt-wtc) and the slope of the straight line resulting from a linear fitting of the data gives the value of the critical exponent, t, equal to 1.41 and a percolation threshold of 0.0071 NC 7000 wt%.

Percolation thresholds lower than this value have been found in literature for heat sheared epoxy systems. Sandler et al. in 2003 found a percolation threshold of 0.0025 wt% using aligned MWCNT, which were relatively straight, unentangled and pure[13]. Martin et al. in 2004[26] again dispersed MWCNT with controlled dimensions, very high degree of purity and alignment in epoxy matrix, obtaining different

percolation thresholds by varying process parameters, with a minimum critical concentration of 0.0021 wt%.

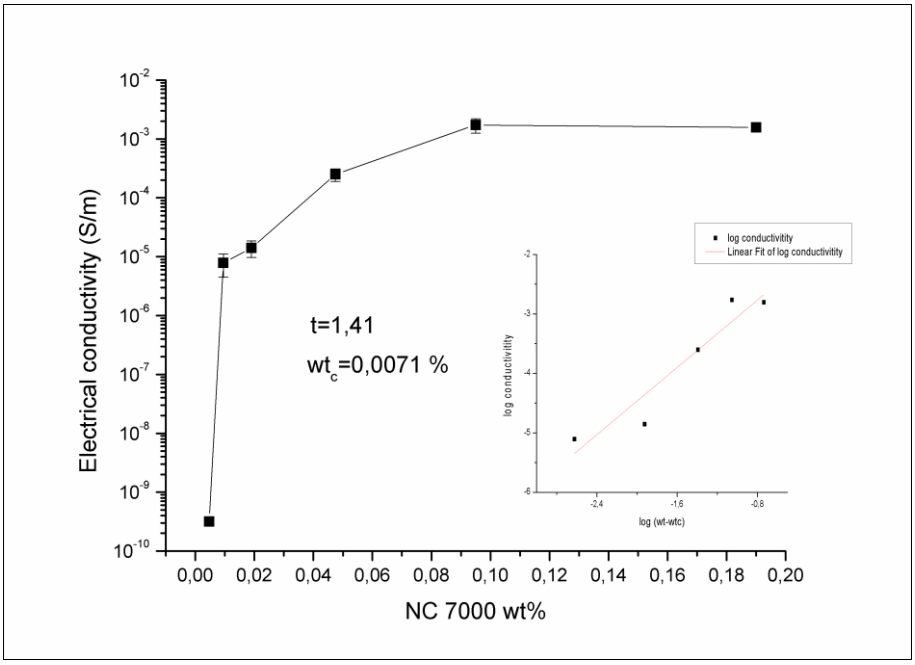


Figure 36 - Percolation curve of the n-EPO composites

Moisala et al. replicated a percolation threshold of 0.0025 wt%, using again non entangled MWCNT, aligned by an in-house CVD method[29]. To our knowledge, it seems that the lowest percolation thresholds found out in MWCNT/epoxy composites have been obtained by using high shear mixing and well aligned, pure and untengangled nanotubes.

In this study, a comparable very low percolation threshold has been obtained by means of high shear mixing as dispersion method as well, but using low purity, entangled, commercially available, very cheap nanotubes as filler[42]. NC 7000 nanotubes are produced in multi-tons, via the Chemical Vapor Deposition (CVD) process, and are considered as an industrial grade material.

The critical exponent t found in this study is comparable to those reported in the mentioned works and it is primarily dependent on the topological dimensionality of the percolating system and not on the details of the structures or interactions[43].

Moreover, its low value does not reflect a reduction in system dimensionality in the present case but rather the aggregation process of the carbon nanotubes during sample preparation[13]. The universal exponent t corresponding to a statistical percolation threshold is equal to 2 and values different from this one are related to kinetic percolation phenomena[44,45]. High values of t correspond to better dispersed composites, while low value to poor dispersion of the fillers within the matrix[45]. In this case, the low value of the percolation exponent is related to the formation of conducting networks of agglomerates, where the percolating element is not the single tube, but the agglomerate. Hence, it is not a true statistical percolation, based on the random distribution of individual high aspect ratio fillers, but rather so low percolation threshold and conductivity exponent are attributed to the mutual attraction of the nanotubes during the curing process[46].

The agglomeration process can be also evidenced by the analysis of the morphology of the composites in optical microscopy images. The dispersion of the tubes appears to be not so fine as it should be if the percolation threshold value had derived from a true statistical percolation phenomenon. In Figure 37and Figure 38 n-composite samples at 0.047 NC 7000 wt% and 0.095 NC 7000 wt% are shown, respectively. The morphology is characterized by a coarse microstructure, with darker area, corresponding to a region with a higher density of tubes, the agglomerates, which contact each other forming a very efficient conductive network within the matrix.

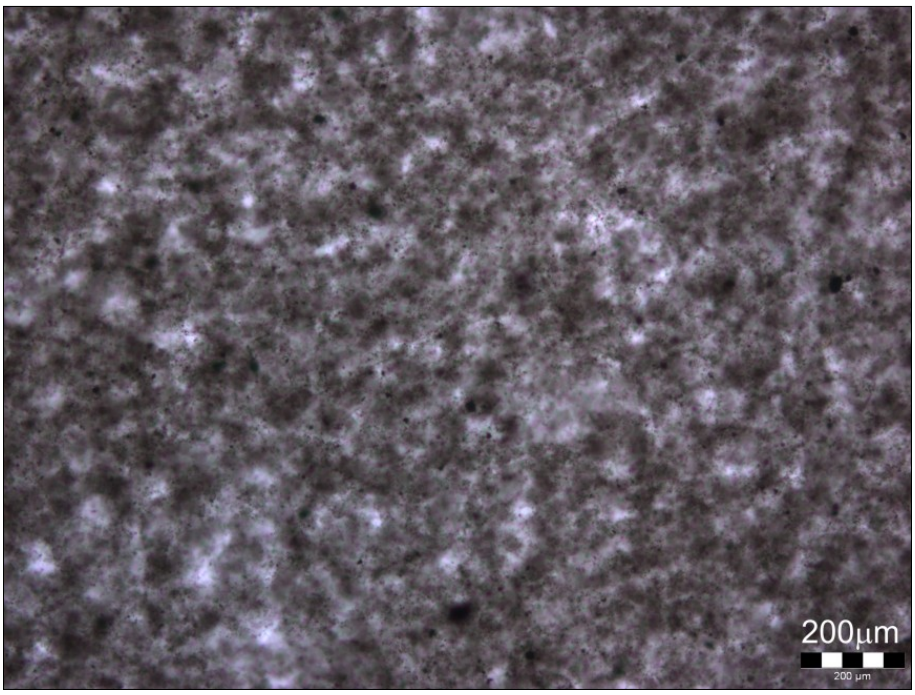


Figure 37 – Microscopy of n-composite sample at 0.047 wt% n-EPO

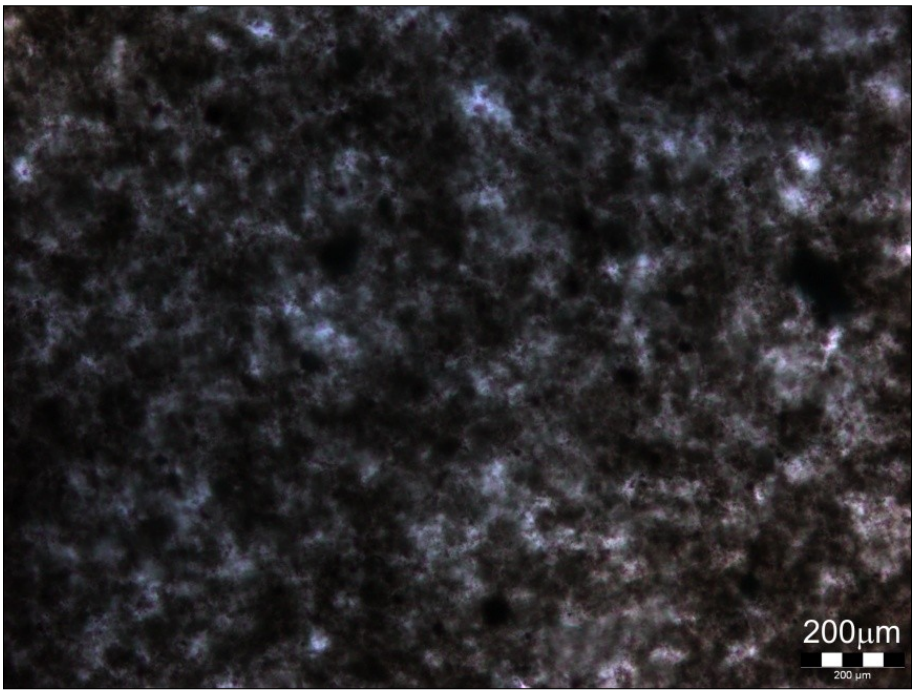


Figure 38 – Microscopy of n-composite sample at 0.095 wt% n-EPO

### 4.4.2 *Electrical Properties and morphology of c-EPO and h-EPO composites*

The addition of functionalized carbon nanotubes to a polymer matrix increases of the percolation threshold of the composite system. The functionalization of CNT surfaces introduces extreme physical and chemical conditions that usually results in defects on CNT surfaces, which strongly impairs electrical properties of pristine nanotubes. As a consequence of the damaging, the stronger are the oxidation conditions the higher the electrical percolation threshold in the nanocomposite[47].

Moreover, because of the increased compatibility between nanotubes and matrix through the presence of functional groups, the polymer wetting of the tubes improves and a higher probability of having insulating matrix between tubes occurs, as opposed to the dispersion of pristine tubes. Without any surface functionalization, CNTs in the composites are still typically separated by a thin layer of polymer matrix material. The thin functionalization agent layers or polymer layers operate as a barrier to the electrical charge transfer between nanotubes[28].

Figure 39 shows the electrical properties of c and h-EPO composites, compared to those already reported of n-EPO composites. Very high concentrations of COOH- and OH-MWCNT in resin don't modify the electrical properties of the matrix, providing almost insulating composites, at content of carbon nanotubes up to 0.95wt%. A slight increase of less than two orders of magnitude in conductivity has been obtained by adding 4.75 wt% COOH-MWCNT to the resin.

For pristine nanotubes (n-EPO) moderately high concentrations still induce dis-homogeneity in the dispersion stage, due to the high increase of viscosity. However, for the production of c and h-EPO composites, the dispersion has been easier and relatively low viscous suspensions have been obtained after the high shear mixing. Due to this high processability the maximum concentration of COOOH-MWCNTs (c-EPO composites) processed was 4.75 wt%. The easier dispersion of those nanotube typologies in EPO resin can be reasonably explained in two ways. Nanotubes after functionalization process are shorter, because of the damaging

induced by the oxidation process, moreover they are free from big catalyst particles, hence they result to be less entangled respect to the pristine tubes and as a consequence more easy to be dispersed. The presence of hydroxyl or carboxyl substituent groups on each nanotubes lead to a solvent effect by the resin. The bisphenols/DGEBA mixture used for the preparation of these composites results very rich of hydroxyl groups, thus becoming like a polar solvent fully compatible with functionalized nanotubes.

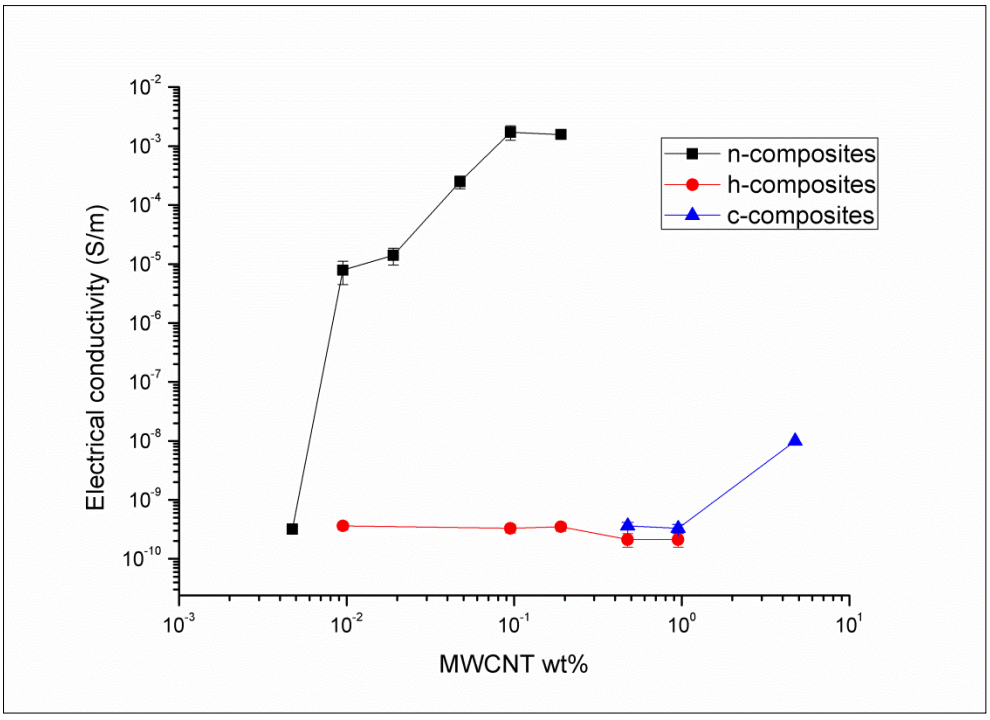


Figure 39 – Electrical conductivity comparison among nanocomposites obtained using MWCNTs pristine (n-EPO) and functionalized (h-EPO,c-EPO)

The low conductivity values obtained for h-EPO composites and the shifting of percolation threshold over the maximum processed concentration (~1%wt) is certainly due to the separation between nanotubes by a thin, non conductive layer of polymer matrix material. Therefore this intimate contact between nanotubes and polymer cannot be explained only in terms of solvent effect, but nanotubes are probably covalently bonded with polymer oligomers, because hydroxyl groups reacted with epoxy rings becoming actual part of the polymer chain.

A very fine and homogeneous dispersion can be appreciated in h-EPO composites by optical microscopy analysis. In Figure 40 a micrograph of the 0.099wt% h-EPO composite is shown and a very homogenous dispersion with a fine texture is visible, with few micrometer sized pristine aggregates, not exfoliated by shearing. Even at higher concentrations of nanotubes, the dispersion maintains its homogeneity, as can be noted in the composite at 0.47 wt%, whose morphology is shown in Figure 41.

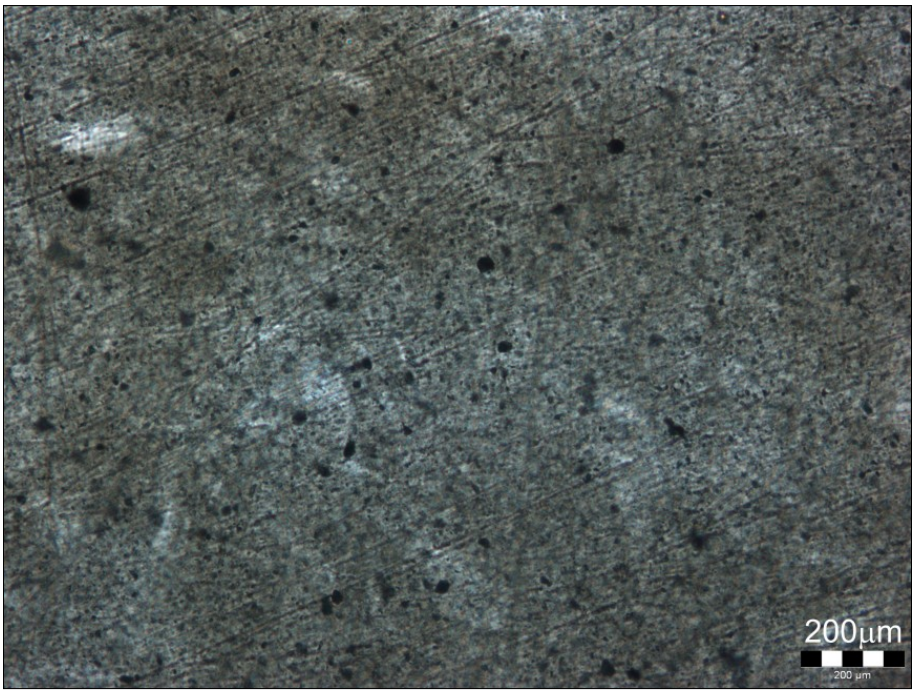


Figure 40 - Microscopy of h-composite sample at 0.099 wt% h-EPO

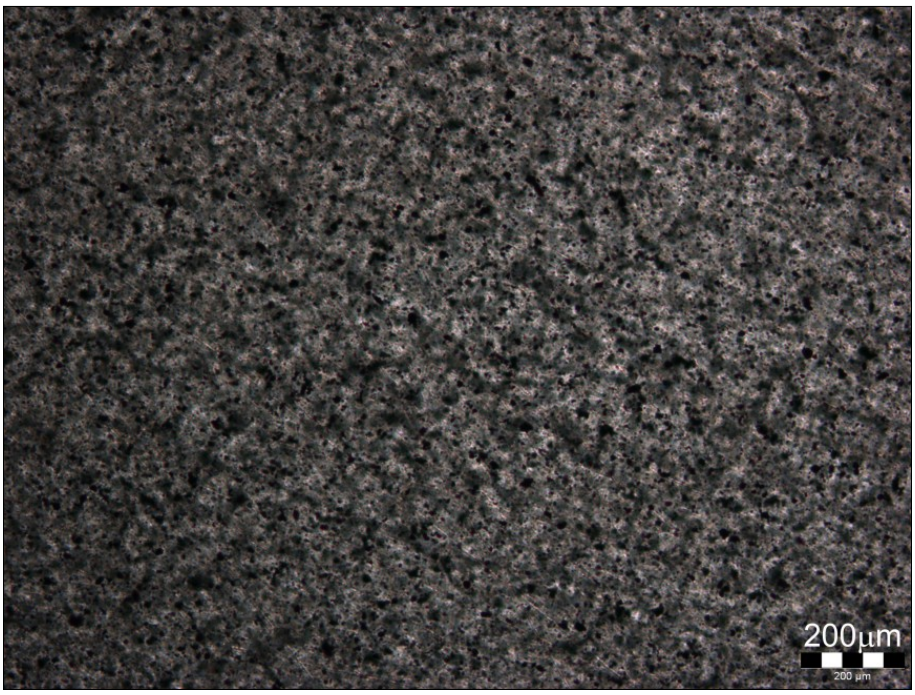


Figure 41 - Microscopy of h-composite sample at 0.47 wt% h-EPO

The comparison between the observed morphologies of pristine nanotubes (Figure 38) and OH functionalized nanotubes (Figure 40) at the same concentration (~0.1%) prove that nanotubes reacted with resin precursors and in the final product are in bulk and they do not provide an actual dispersion within the polymer matrix.

A different dispersion state can be observed in c-EPO composites (Figure 42), where a less homogeneous dispersion of the nanotubes characterizes the samples respect to the h-EPO composites. It seems that nanotubes are not well disperse within the resin and they remain as aggregates of pristine bundles not exfoliated. A different explanation can be provided: during polymerization carboxylic groups react with epoxy ring by releasing water molecules. This occurrence dramatically changes the polymerization process, inducing an inefficient polymerization in the bulk material, followed by a decreasing of Tg, due to the presence of small quantities of by-products, which cause matrix softening and segregation, with the occurrence of multiple phases. Hence, even if mixing stage had efficiently dispersed nanotubes, during polymerization, they would re-aggregate by differences in miscibility in the different phases originated by the segregation.

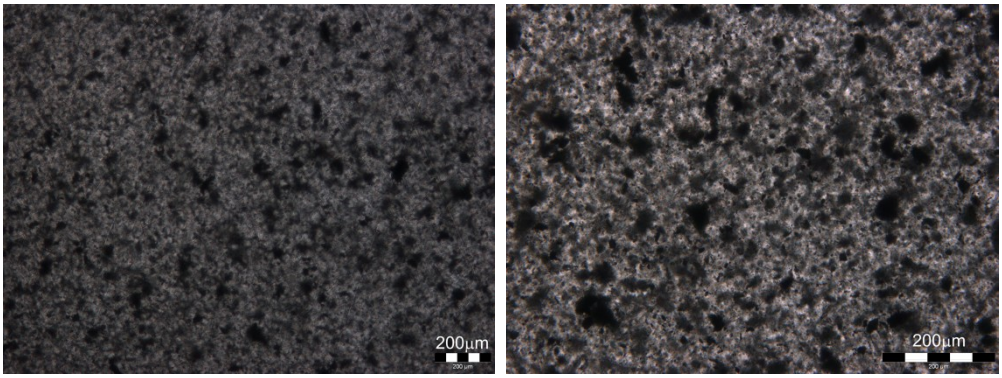


Figure 42 - Microscopy of c-composite sample at 0.47 wt% COOH-MWCNTs (left 5x, right 10x)

### *4.4.3 Mechanical Properties of thermoplastic Epoxy/CNT nanocomposites*

Dynamical mechanical tests were carried out using a DMA Q800 TA Instruments in Single Cantilever bending configuration over a temperature range of -20°C to 150°C performed with a rate of 3°C/min. Preliminary strain sweep tests were performed on the neat system to set test parameters, the linear behavior region were investigate in order to have mechanical measurements reliable over all the temperature range. For statistical purpose, at least three different samples with nominal size of 40 x 10 x 2 mm (±0.1 mm) were cut from each manufactured plate by precise diamond sewer machine and they were tested at constant maximum tensile strain of 0.10% .

DMA test carried upon the neat system is already reported in chapter 3 (see Figure 33), the neat system exhibits in the transition region a loss modulus greater than the storage modulus confirming its thermoplastic behavior, with a transition temperature of about 95 °C.

DSC measurement performed upon the n-EPO nanocomposites show an increment in the transition temperature (Figure 43) of nanocomposites respect to the neat hosting system, moreover at nanotubes content greater the percolative one the nanocomposites exhibits a slightly variation in the transition temperature. As reported in the following figure the nanocomposite containing 0,005%wt of

nanotubes is the boundary between two different material behaviors, this latter occurrence is attribute to a progressive growth of nanotubes-based structures within the hosting matrix which is triggered when a connected path is established. The n-EPO nanocomposite family displays the triggering effect on the transition temperature a nanotubes content equal to the critical percolative content according to the previous reported electrical measurements.

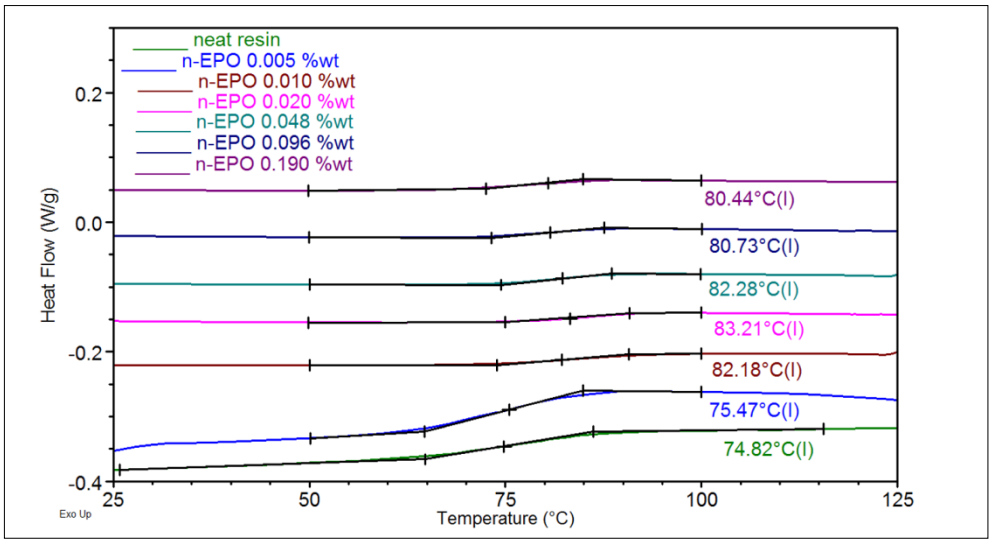


Figure 43 - n-EPO, Transition temperature as function of nanotubes content. DSC measurement

The following table reports mechanical properties of *n*-EPO nanocomposites at room temperature. With the aim to investigate the reinforcing effect of nanotubes within the hosting system the volume content of carbon nanotubes is evaluated from their weight percentage, nanotubes and resin density. Figure 44 shows the increment in bending modulus for nanocomposites at increasing nanotubes content, mechanical data highlight a non linear relationship between composite elastic modulus respect to the filler content. This latter phenomenon is well-known in literature[1] since the reinforcing effect of nanotubes depends not only in their amount within the composites, but also in their state of dispersion and by the dimension of micro-sized agglomerated growth during the dispersion stage.

Coleman[4] suggested to investigate the reinforcement effect of carbon nanotubes within an hosting system by means of their effective modulus, that is the increment in material stiffness divided by its amount, as general rule the maximum value is expected at dilute regime since isolated "*tubes*" has got the maximum efficiency in load transferring. Table 9 reports still the effective reinforcement modulus of filler for n-EPO composites, the lower the nanotube content the maximum the effective reinforcement modulus have been measured (1.1 TPa), in dilute regime carbon nanotubes could be considered isolated within the hosting matrix, that is its reinforcement effect tend to the stiffness of the single nanotubes (few TPa)

Table 9 - *n*-EPO: Bending modulus and Effective reinforcement modulus measured by DMA test extrapolated at 25°C

| % w/w | % vol | E (MPa) | $E_{Dev.st}$ | Eη (GPa) |
|---|---|---|---|---|
| 0,000 | 0,0000 | 2070 | 109 | - |
| 0,010 | 0,0076 | 2154 | 84 | 1107 |
| 0,020 | 0,0152 | 2135 | 3 | 431 |
| 0,048 | 0,0364 | 2234 | 123 | 454 |
| 0,096 | 0,0728 | 2300 | 50 | 318 |
| 0,190 | 0,1440 | 2375 | 215 | 214 |

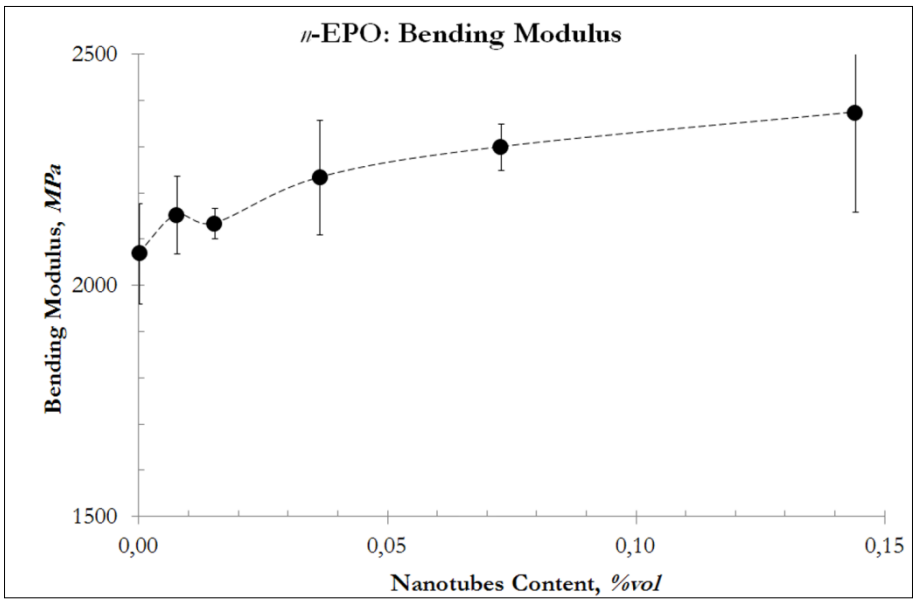


Figure 44 - n-EPO, Bending modulus at room temperature vs Nanotubes content . DMA measurement

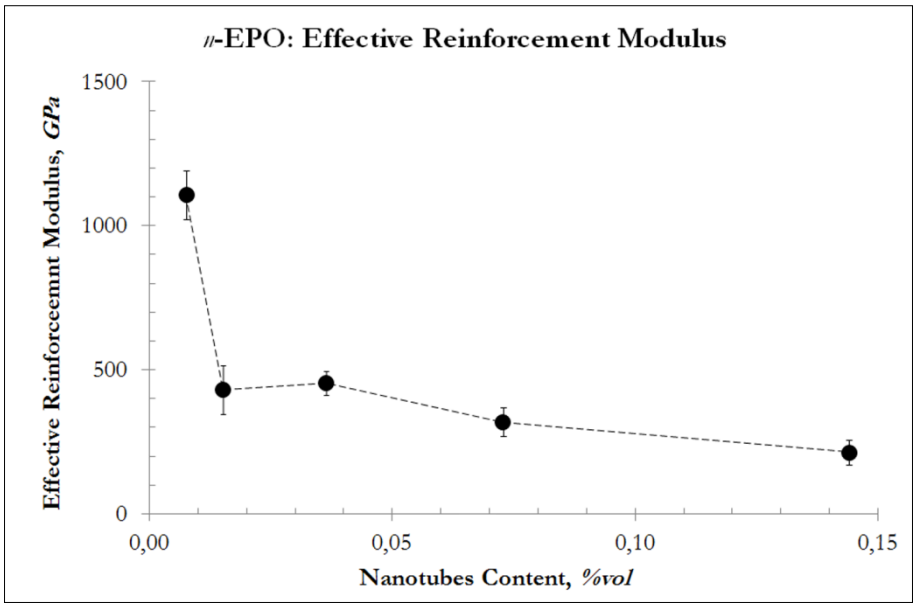


Figure 45 – n-EPO, Effective Reinforcement Modulus vs Nanotubes content

Figure 45 shows the effective reinforcement, Eη as a function of the nanotubes content in volume percentage. Reinforcement efficiency decreases monotonically from the value of 1107GPa at 0.0076%vol to 214GPa at 0.144%vol with nanotubes content increasing. Two limiting behaviours have been identified. They are

separated by the onset formation of a nanotube percolative network: below the percolation threshold, reinforcement efficiency tends to values typical for the single nanotube Young modulus (of the order of few TPa) while, above the percolation onset, effective reinforcement drops to values of the order of one undred GPa.

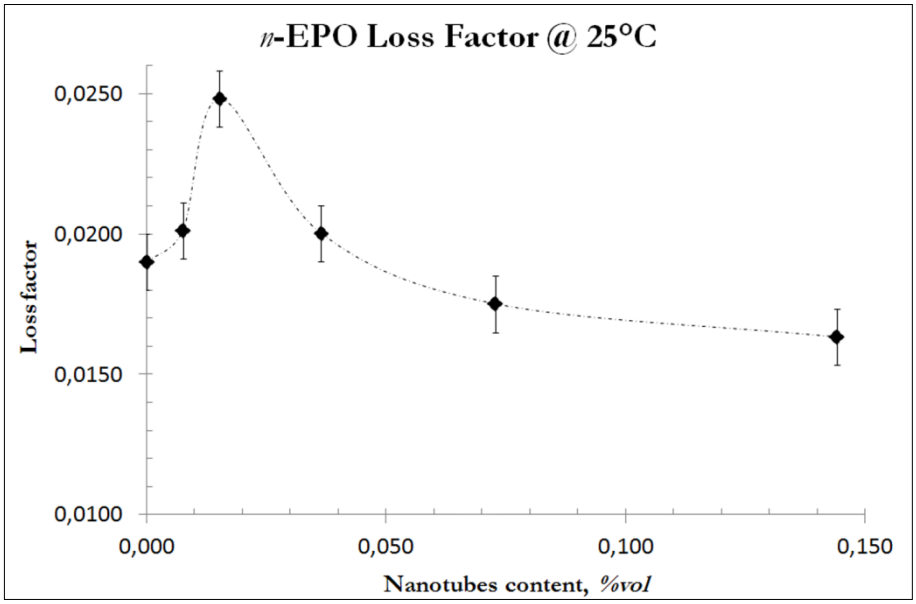


Figure 46 - n-EPO: Loss factor vs. nanotubes content

Figure 46 reports the loss factor as function of the nanotubes content; the progressive formation of a connected path within the material led to two opposite behavior triggered when the percolative content is accomplished. This latter phenomenon could be the key of a new generation of composite materials, in fact in the dilute regime, the addiction of nanotubes to the hosting system allow to catch the maximum efficiency in reinforcing the matrix with an increase to the dissipative performance of the material.

The functionalization of carbon nanotubes dispersed within the thermoplastic epoxy system significantly affects the micro-sized morphology of the final nanocomposites. In fact, optical images reveal (according to Figure 40) that the presence of functional hydroxyl group –OH, shift to higher content the percolative network formation, as already reported in the previous paragraph according to the experimental results of electrical conductivity. Therefore, it seem reasonable to

assume that the –OH group had interacted with precursors during the polymerization stages, thus the conductive percolative network could not be formed. Moreover, the effect on glass transition temperature could be consider negligible compared to n-EPO samples. This is well represented by results obtained using DSC (Figure 47) DMA (Figure 48 and Figure 49): the only evident difference among neat resin and h-EPO nanocomposites is represented by a decrement of tanδ, probably, due to a reduction of molecular mobility. The reduction of bending modulus at higher concentration of functionalized nanotubes is due to the stoichiometric unbalance caused by the excess of hydroxyl groups.

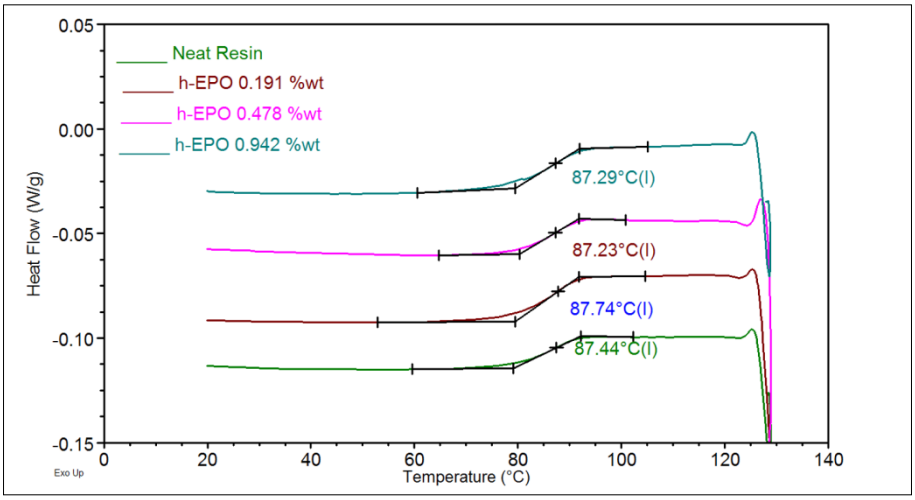


Figure 47 - h-EPO, Transition temperature as function of nanotubes content. DSC measurement

The experimental results (Figure 50 and Figure 51) by DMA and DSC on c-EPO lead to further fundamental considerations regarding the effect of functional groups and their potential interactions with the hosting system. The significant increasing of the percolation threshold at 4.75%wt induces a stoichiometric unbalance of the bulk system polymerization and furthermore, the formation of water molecules as residues could be acting as plasticizer lowering the effect on glass transition temperature.

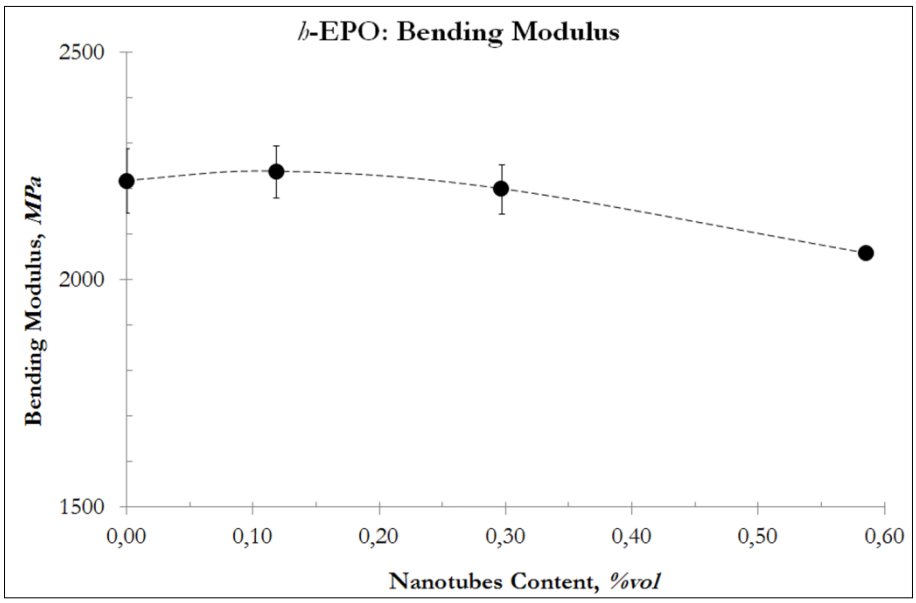


Figure 48 - h-EPO, Bending modulus at room temperature vs Nanotubes content . DMA measurement

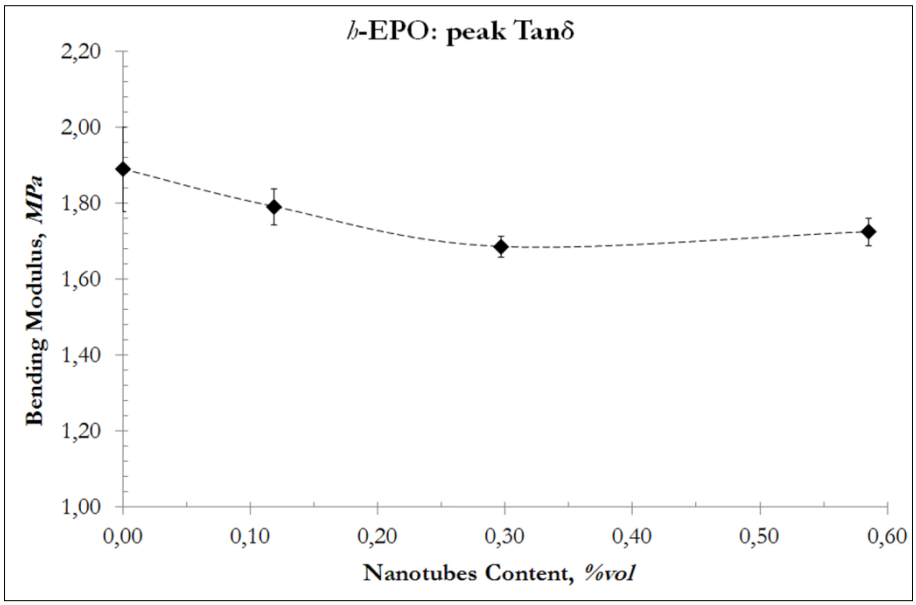


Figure 49 – h-EPO tand peaks as function of nanotubes content

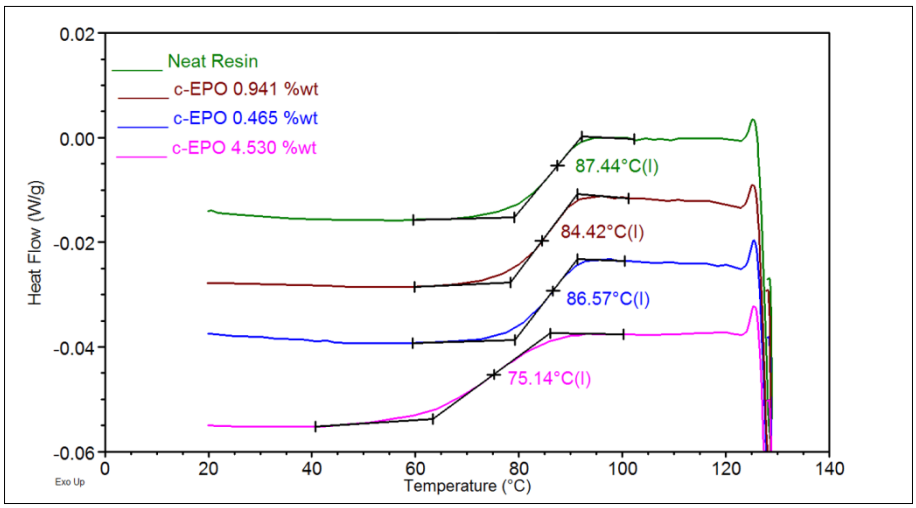


Figure 50 - c-EPO, Transition temperature as function of nanotubes content. DSC measurement

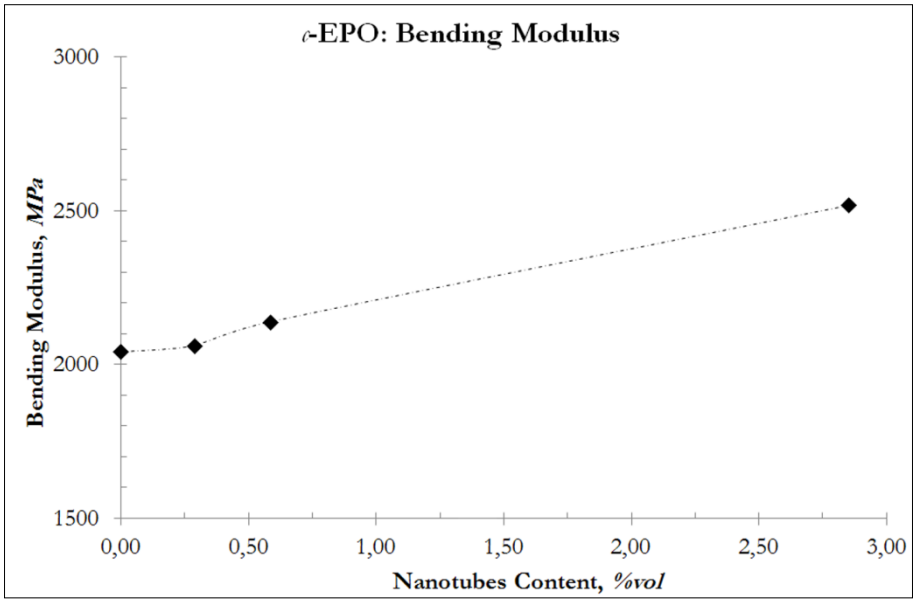


Figure 51 - c-EPO, Bending modulus at room temperature vs. Nanotubes content . DMA measurement.

### *4.4.4 Modelling nanocomposites mechanical behaviour*

In spite of the outstanding mechanical properties of single tubes, long fibre reinforced nanopolymer composites exhibit a very limited improvement of mechanical performances, if compared to conventional advanced composites. This contradictory behaviour can be explained by considering that the reinforcing

contribution of carbon nanotubes is yielded not only by their amount within the material, but also by the state of dispersion, orientation, shape and number of contacts within the hosting system. All these features play a critical role on the final reinforcement enhancement, and they should be taken into account to develop reliable models for prediction of nano-composite effective properties.

Since CNTs could be assimilated to "tiny" short particles, the classical micromechanics approaches for short fibre reinforced composites (SFRC) were employed as first attempts to develop predictive models of CNT/polymer composites[4, 7].

In this paragraph is reported a briefly description of a recent attempt to include the connectedness of tubes and the waviness feature of the carbon nanotubes within the hosting medium. The main achieved results, experienced on CNT/nano-composites by many researchers, could be correctly summarised as follows:

1) the dependence of the effective reinforcement modulus upon the tubes aspect ratio. In the very dilute regime the effective elastic modulus of CNT depends directly on the averaged aspect ratio of the filler.

2) the reduction of mechanical efficiency at increasing volume content. As the nanotube content increases due to the progressive increment of tube-to-tube contacts the effectiveness of transferring load decreases.

Shear-lag-based approaches have been widely used to analyse the effect of the aspect ratio on mechanical of carbon nanotubes composite. The main assumption of these models is the perfect adhesion between the phases where the stress transfer occurs via a shear mechanism. By applying the shear lag models, the composite modulus results an average value of the specific components modulus that are reduced by a numerical factor depending on the aspect ratio of the reinforcing filler. In this case, the most prominent expression for the prediction of the nano-composite Young's modulus is given by equation (3).

$$
\begin{aligned}
E_c &= E_\eta \cdot \phi + E_m \cdot (1-\phi) \\
E_\eta &= \eta \cdot E_{NT} \\
\eta &= 1 - \frac{\tanh(K \cdot AR)}{(K \cdot AR)} \\
K &= \sqrt{\frac{-\frac{2}{1+\nu_m}}{\frac{E_{NT}}{E_m} \cdot \ln(\phi)}}
\end{aligned}
\tag{3}
$$

The stress transfer parameter, K, is computed, according to the Carman-Reifsnider assumption, considering, as fibres arrangement, a cylindrical packing surrounded by the matrix. While the progressive formation of contacts among tubes creates a fully connected web which improves the materials conductive (thermal and electrical) behaviour, the mechanical performances are characterized by an opposite tendency. Actually, contacts among the "tubes" create points at which negligible load transfer could be assumed. Therefore, a predictive model for such nano-composites needs to account for arising number of contact points with the CNT content.

The Random Contact Model is based on the assumption that two particles of any shape can contact with a probability which is averagely independent on other contact formations, in other terms, if contacts are uncorrelated, their number for each particle varies linearly with the particle concentration. The theory states that the average number of contacts per particle <c> is dependent on the normalized average excluded volume, Vex, and the particles volume fraction, φ, according to the following expression:

$$
\langle c \rangle = \varphi \cdot \frac{V_{ex}}{V_p}
\tag{4}
$$

Contacts between nanotubes imply a reduction of the stress transfer efficiency of the reinforcement, afterwards the rule of mixtures could be modified by reducing the stress transfer coefficient by the average number of contacts

$$\eta = 1 - \frac{\tanh\left(\frac{K \cdot AR}{1+<c>}\right)}{\left(\frac{K \cdot AR}{1+<c>}\right)} \qquad (5)$$

The latter method is able to describe the reinforcement effect of nanotubes as function of only two physical parameters: their aspect ratio and their curliness, compared to other attempts to model nanocomposites stiffness the chosen approach does not require the introduction of parameter with weak physical meaning.

Figure 52 reports the comparison between *n*-EPO experimental data and model prediction, as displayed by this picture the model is capable to describe the non linear dependence of elastic modulus from nanotubes content.

The best fitting parameters report an effective aspect ratio of 90 and a curliness factor of 12.3, values compatibles with nanocomposites fillers.

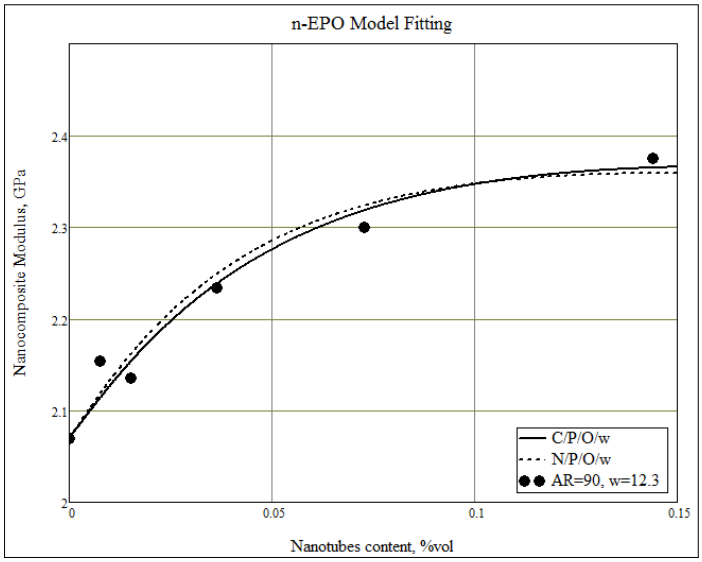


Figure 52 - n-EPO, Comparison between experimental data and the model prediction

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# 5.

# FIBER REINFORCED POLYMER MATRIX COMPOSITES

## 5.1 Summary

In this chapter, the manufacturing processes for fibre reinforced polymer matrix composites were analysed focusing on suitable techniques which can be useful to manufacture reactive thermoplastic polymers.

The early paragraph is dedicated to a description of processes already used to for manufacture parts and components by using reactive processing of non-epoxy thermoplastic or thermosetting epoxy resins. Differences between processing of thermosets and thermoplastics are highlighted and briefly described.

Following, a detailed description of the process performed to manufacture a 2D fiber reinforced composite element by reactive processing, using EPO formulation is presented and described. Test carried out of cut specimens from this elementary structure were also reported and analysed.

A proof of feasibility and effectiveness of the reactive processing by EPO product and the reshaping potentiality after polymerization of the long fiber reinforced system can be surely considered as the main achieved result of the work presented in this chapter.

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## 5.2 Reactive processing of textile reinforced thermoplastic composites

In this section, four reactive processes to manufacture textile fiber-reinforced TPCs are presented: structural reaction injection molding, vacuum infusion, resin film infusion (see Figure 53) and pre-preg technology. Reactive processes for neat polymer parts like casting, reaction injection molding (RIM) and rotational molding, and for short fiber reinforced composite parts like reinforced reaction injection molding (RRIM) are described in literature, as well as reactive injection pultrusion (RIP) of continuous fiber-reinforced profiles.[1]

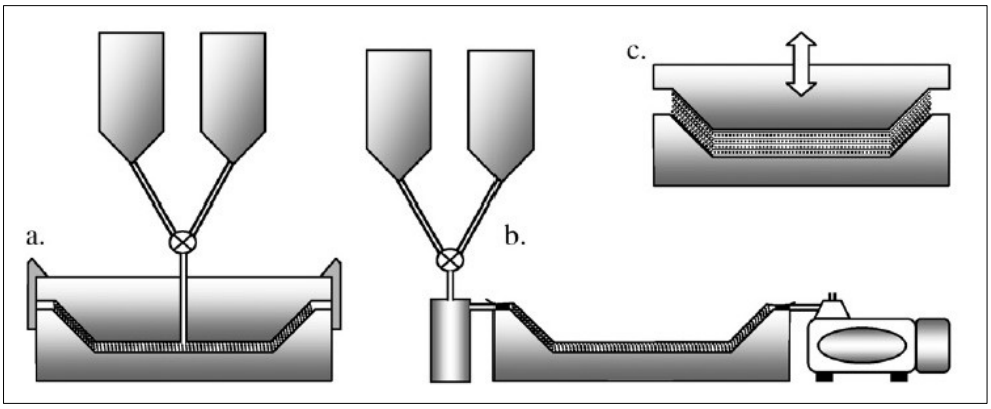


Figure 53 - Schematic representation of three reactive processes for manufacturing of thermoplastic composites: (a) structural reaction injection moulding (SRIM), (b) vacuum infusion (VI) and (c) resin film infusion (RFI).1

### *5.2.1 Structural reaction injection molding (SRIM)*

SRIM uses high pressure (8–10 bar) to impregnate a dry fiber pre-form positioned between two solid mold halves[2, 3, 4] (Figure 53a), The process is directly associated to Resin Transfer Molding (RTM) of thermoset composites. To achieve a proper fiber impregnation, low viscosity reactive mixtures are required and 1 Pa·s is usually considered as the upper processing limit of the reactive mixture viscosity. Upon conclusion of polymerization, the composite part can be demolded. As the size of the product increases so does the clamping force required to keep the mold closed during injection of the resin. As a consequence, the size of parts manufactured through SRIM is limited. The reactive mixture is prepared at moment and

precursors are separated into two material feeds, in order to prevent premature polymerization. Just before entering in the mold, the material feeds from two tanks are efficiently mixed and polymerization starts. The big advantage of SRIM is the fast cycle time, whereas the high tooling costs are the main disadvantage.

### *5.2.2 Vacuum infusion (VI)*

As the name suggests, vacuum is used to compact and impregnate a dry fiber pre-form, which is placed between a solid mould and a flexible bag, see Figure 53b.[1, 5, 6, 7]. Although the impregnation times are higher, if compared to SRIM and the fact that atmospheric pressure is sufficient for mold clamping lead to that the maximum achievable part size is only limited by the pot-life of the reactive system. After mixing the reactive mixture (maximum viscosity: 1 Pa·s) is dispensed into a buffer vessel, which is required to separate the pressure required for dispensing and the vacuum necessary to promote infusion. The big advantages of VI are the virtually unlimited size of the parts that can be produced and the low cost tooling due to the low pressures involved. The disadvantages are related to the flexible mold half, which often can be used only once and leads to a poor surface quality on one side of the product.[1]

### *5.2.3 Resin film infusion (RFI)*

RFI is analogous to pre-pregging of thermoset composites: hand lay-up is used to stack alternating layers of fibre textiles and sheets of unreacted reactive mixture in a mould, see Figure 53c. Upon applying heat and pressure, resin sheets melt and impregnate fibres, after which polymerization initiates. In case the sheets do not have sufficient mechanical properties for handling, they can be directly cast on top of a supporting fibre textile. Also powder impregnated textiles can be used. To maintain reactivity, no premature solid-state polymerization or deactivation during storage or handling of the unreacted sheets or pre-pregs should take place. During melting and impregnation a significant volume reduction of the lay-up takes place and often several de-bulking steps are necessary to compress the lay-up. The atmospheric pressure is typically adequate for de-bulking of thin-walled parts and

allows the use of a flexible half-mould. In this case, the viscosity of the reactive mixture is again limited to 1 Pa s. De-bulking of thicker parts is more difficult and often required a second solid half-mould and significant pressure, which simultaneously allows the use of oligomeric precursors with a higher melt viscosity. The simplicity of preparing the lay-up and the fast impregnation are regarded as the main advantages of RFI, whereas de-bulking is the main disadvantage.

### *5.2.4 Out of autoclave Pre-pregs*

A prepreg is produced by impregnation of a reinforcement fabric with a reactive pre-mixed formulation. No liquids are handled after this step. The matrix in the prepreg is, in a so-called B-stage, an ungelled liquid of very high viscosity, but with the necessary tack, flexibility and shelf life to facilitate part manufacturing. There are different ways to impregnate the fabric and reach the B-stage. In the chemical B-stage, to allow a good impregnation the viscosity is reduced by heating, then a partial polymerization reaction occurs, to reach an appropriate conversion below gelation. In the physical B-stage, the so-called hot melt process is carried out by impregnating reinforcements at high temperatures, to reduce viscosity, followed by cooling to reach the initial viscosity at room temperature. The alternative is the use of a solvent in the formulation to facilitate impregnation followed by its removal in a drying tower. These processes lead to homogeneous prepregs with constant fibre content. This allows production of constant high-quality composites. Final parts are produced by placing prepregs in a mould with the required stacking sequence, and curing in a heated press or in an autoclave under temperature and pressure.

Production of parts from prepregs requires expensive bagging films and autoclaves or presses. In order to reduce production costs but still make high quality parts pre-preg some manufacturers developed different technologies. In some techniques these materials consist of a layer of fibre reinforcement either side of a precast, pre-catalyzed resin film, with a light tack film on one face. Unlike conventional prepregs, the fibres remain dry and unimpregnated by the resin until the curing process. This gives these materials their outstanding breathability, and enables one to achieve autoclave-quality laminates from vacuum bag processing. Heat and

vacuum activate the resin flow and enable the infusion of the reinforcement. These technologies provide a quick and cost-effective way of producing large and thick laminates, ensuring full impregnation of the reinforcement. Some relevant features of this process are: easy positioning of the plies in the mould due to the high resin content of the tacky face; easy re - positioning of plies due to the dry face, especially in the case of large structures; reduction of voids to a minimum due to the easy draining of air and volatiles. However, the price of the materials is higher than those used in processes based on liquid resin infusion This technology is a good alternative to RFI ( resin film infusion ).[8]

### *5.2.5 Differences between reactive processing of thermoplastic and thermosetting composites*

Reactive processing of thermoplastic composites seems to have a lot in common with manufacturing of thermoset ones. There are however a few significant differentiations, which are summarized briefly as follows:

- both for thermoplastic and thermosetting resins, the polymerization rate increases with temperature arising. However, when the processing of reactive thermoplastic materials with a semi-crystalline nature is performed, temperature effects on crystallization needs to be taken into account. The processing temperature has to be chosen such that polymerization and crystallization results well balanced. When the temperature is too low, crystallization will be too fast and reactive chain ends, consequently monomer can get trapped inside crystals before they can polymerize. On the other hand, when the temperature is too high, the final degree of crystallinity is lowered, reducing in turn the strength, the stiffness and the chemical resistance of the polymer system[7].

- some reactive thermoplastic materials, like PA-6, PA-12 and PBT, have a melt viscosity, which is an order of magnitude lower than of common thermosetting resins. As a consequence, the occurring capillary forces

during impregnation of the fibre pre-form are significant and form a potential source for voids and runner formation.[1]

- while many thermosetting resins are liquid at room temperature, most thermoplastic precursors are still solid. Heated equipment is therefore necessary to keep the unreacted mixture in the melt state.[1]

- De-moulding techniques that make use of the brittle nature of thermoset resins, such as peel plies in vacuum infusion and break lines through resin rich areas, are not fully applicable due to the tough nature of the thermoplastic material.

- The performance of composites are in not only determined by the fibres and the matrix, but also by the fibre-to-matrix interphase. To improve adhesion, glass fibres for instance are usually coated with silane coupling agents: di-functional compounds with the capability to bond with both the fibres and a polymer matrix of choice. A non-compatible coupling agent results in a weak interphase or even prevent the polymerization of reactive resins. Coupling agents have been developed for numerous thermoset composites resins and for thermoplastic composites manufactured through melt processing. Coupling agents specifically for reactive processing of thermoplastic composites have not been developed yet, but have recently become a topic of interest.[1]

- In addition to fibres with suitable coating, processing aids for, for instance, vacuum infusion of thermoplastic resins such as transport tubes, vacuum bagging films and sealant tape are not commercially available as such. Suitable high-temperature consumables, which are chemically resistant against the unreacted thermoplastic materials, therefore still need to be selected.

Perhaps the most striking difference is the fact that whereas reactive processing of thermoset composites forms the mainstay of the composite industry worldwide, the potentially great of thermoplastic resins have not found any significant composite

application so far. This cannot be related to the expected properties of reactively processed thermoplastic composites, given the fact that their melt-processed equivalents have already found extensive application.

## 5.3 Reactive processing of a fibre reinforced composite using EPO system

In order to prove the process capabilities of the developed thermoplastic epoxy-based reactive system an effective manufacturing test has been carried out. Among reactive processes described above one technique has been selected. Then, the processing test has been performed by manufacturing some prep-preg sheets, which were, subsequently, used to realize a plane composite laminate. To consolidate the 2D composite laminate, an hybrid technique "inspired" to vacuum infusion process has been used, in order to use pre-preg in an out-of-autoclave process. The final component has been basically tested to proof the reshaping potentially of the system along with mechanical property and resin content.

### *5.3.1 Materials*

The thermoplastic epoxy-based system (EPO) used has been well described in previous chapters. The process parameters has been set up according to guidelines described at the end of chapter 3.

Selected reinforcement is a plane textile reinforcement, made by unidirectional carbon fibers, manufactured by Hexcel and coded as G1157.

### *5.3.2 Pre-preg manufacturing*

Then unreacted EPO resin has been previously catalyzed and then heat up to 80-90°C to reduce viscosity and facilitate textile impregnation. The entire impregnation process has been carried with a strictly control of temperature (<100°C), in order to prevent any pre-polymerization occurrence. Pre-pregs were produced with a controlled excess of resin, in order to improve adhesion during stacking procedure,

then a calendering stage was used to control the amount of resin applied to the textile reinforcement. Once impregnated pre-preg was cooled and stored.

### *5.3.3 Plate manufacturing*

For the plate manufacturing a VI process-like has been used. Pre-preg laminas have been placed by hand lay-up on a solid preheated half-mould. The mould has been preheated at 80°C, in order to thin the resin in the pre-preg and make it more tacky. Every lamina has been slightly preheated, then it has been stacked according the lamination sequence [0/90/0/90/0], in order to obtain a cross-ply symmetrical laminate (see Figure 54).

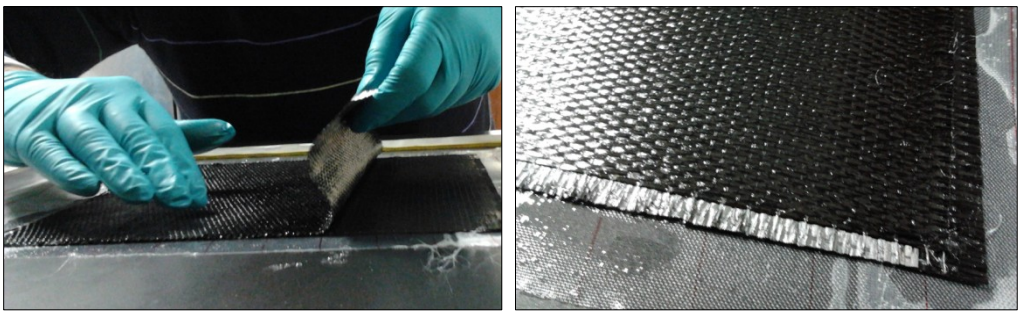

Figure 54 – Prepreg hand lay-up (sx) and stacked laminate (dx)

Once all laminas have been stacked, stripes of breather fabric have been placed on the surroundings of prepregs, then a peel ply and a vacuum bagging film have completed the curing bag. A vacuum valve was mounted in order to apply negative pressure to compact and promote the absorption of the resin excess by breather fabric (see Figure 55). Once the absence of vacuum loss was verified the polymerization cycle was carried out, according to the optimized cure schedule reported in chapter 3. In Figure 56 is clearly shown the excess of resin absorbed by breather fabric.

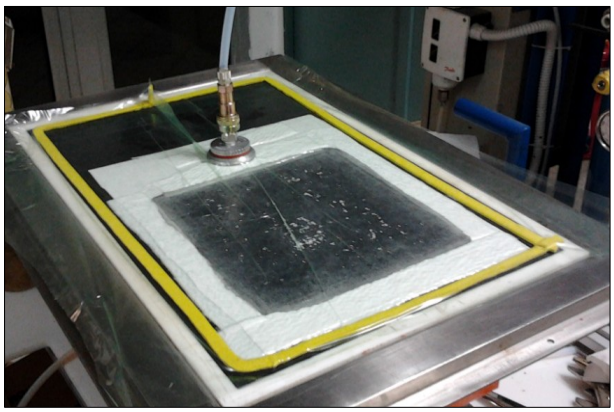

Figure 55 – Curing bag assembled

Once the polymerization schedule was concluded the part was allowed to cool down under natural convention.

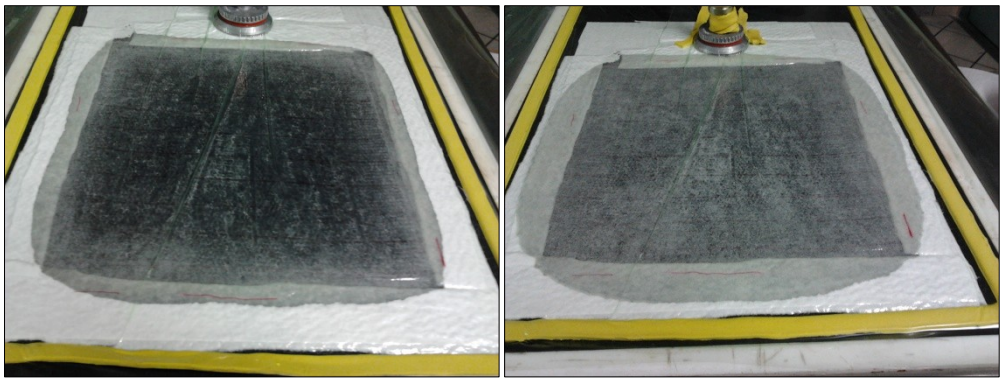

Figure 56 – Plate curing: in evidence resin excess which flows in the breather

### *5.3.4 Preliminary testing*

The manufactured plate did not exhibit evident, visual defects, only an high surface roughness, due to the inappropriate peel ply, which resulted excessively porous, compared to the effective fluidity of resin.

The first preliminary test which has been carried out was the evaluation of the final volumetric fibre content (71%). Then tensile test in the first principal direction has been performed: the laminate Young modulus was 67±1GPa and the ultimate strength was 555±25 MPa. Tested specimens were affected by slightly fiber misalignments, probably due to the hand lay-up manufacturing. A further test

performed on strips cut from the manufactured plate was the hot forming reshaping. Rectangular specimens have been preheated over the glass transition temperature and shaped in the rubbery state using a bending load (see Figure 1 and Figure 2).

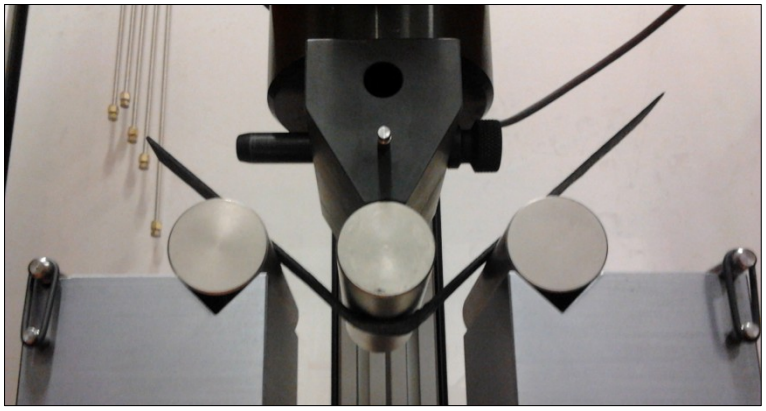

Figure 1 - Preheated laminate specimen shaping using bending load

Specimens reported in Figure 2 shown that the realised resin product can be suitably reshaped above its glass transition as a common thermoplastic material even though its mechanical performance are very resembling a thermosetting resin system.

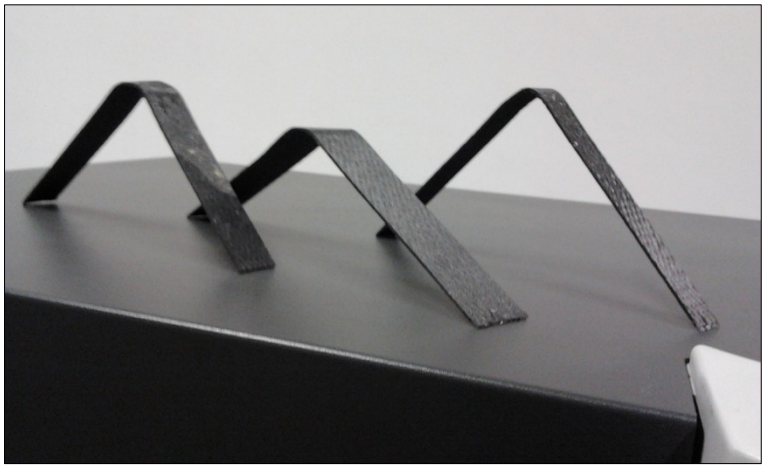

Figure 2 – Shaped specimens

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# 6.

# CONCLUSIONS AND PERSPECTIVES

## 6.1 Conclusions

The presented research work was carried out to achieve tow main results: the development of a thermoplastic epoxy-based system which can be reactively processed and its application to manufacture epoxy/CNT nanocomposites and fibre reinforced composites.

The state of the art on thermoplastic composites manufactured by reactive processing was presented and discussed, in order to bring into focus materials and processes, for which was developed a capable, integrated and optimized reactive processing. By merging the available know-how for epoxy-based thermosetting matrices and the experiences reached by the development of reactive thermoplastic systems, guidelines for material designing were developed and proposed.

According to these guidelines, the down selection process of material precursors was carried out and a thermoplastic epoxy-based reactive system (labelled EPO) was produced and characterized.

Polymer nanocomposites have been introduced, in particular epoxy/carbon nanotubes composites and various approaches to improve the dispersion, orientation, and adhesion of CNTs were reviewed. The nanocomposites manufacturing by the thermoplastic epoxy-based reactive system formerly developed was carried out. The resulting nanocomposite properties are described, by focusing on electrical and mechanical features.

Finally, the manufacturing processes for fibre reinforced polymer matrix composites was set and developed; moreover, a fibre reinforced demonstrator was realized by reactive processing by using the formulation formerly developed. The

proof of feasibility and effectiveness of the reactive processing of EPO product and the reshaping after polymerization of the reinforced has been carried out.

## 6.2 Future Works

All results achieved during this work can surely be enhanced at different level.

The thermoplastic epoxy-based reactive system produced and characterized could be enhanced, i.e. by increasing mechanical (ultimate properties) and thermo-physical properties (Tg), in order to reduce the performance gap between thermosetting and thermoplastic epoxy products. However, optimization should be carried out to preserve the processability of these systems by means of traditional manufacturing technique.

Within the frame of carbon nanotube filler to enhanced the property of the developed system, indeed, the chemical interaction among reactive polymer and nanotubes should be better investigated in order to maximise the synergistic effects of carbonaceous nanostructures. Moreover, different typology and structures of carbon nanoparticles could be investigated along with their effects of some other interesting specific property such as flame retardancy, thermal property and degradation kinetics.

Processing of this novel class of materials should be further optimised to scale up the process reliably at industrial level.

## 6.3 Curriculum Vitae

Angelo Petriccione was born in Caserta, Italy, on the 9th July 1979.

He received the bachelor degree in Materials Science and Engineering in 2004 with 100/100, with a thesis dissertation on modelling of thermal phenomena in materials used for aeronautical de-icing systems. In 2006 he obtain the master degree in Materials Engineering with 100/100 cum laude, with a thesis dissertation on numerical models to describe micromechanical damages induced by dynamic thermal loads on Fiber Metal Laminates.

Since 2005 he has been collaborating with Italian National Research Council, at Institute for Composite and Biomedical Materials (IMCB) working mainly on reinforced polymer composites. He participated as consultant to many research project involving applications of composite materials in structural, automotive and aerospace fields.

He starts his Ph.D. program in 2009 addressing his research activities on reactive processing of thermoplastic epoxy based system and its application in epoxy/CNT nanocomposites and fibre reinforced composites.

Her main research interest field is set in the context of advanced composites materials.

## 6.4 Academic Publications

| | **Journal Articles** | |
|---|---|---|
| **1** | Structural polymer composite materials for muscle-skeletal diagnostic systems<br>M.F. Pernice,D. Annicchiarico, A. Petriccione, G. De Tommaso,M. Meo, V. Antonucci, M. Zarrelli | **Journal of Reinforced Plastics and Composites** |
| **2** | A stiffness volume averaging based approach to model NCF reinforced composites<br>A. Petriccione; D. Annicchiarico; V. Antonucci; M. Giordano;A. Riccio; F. Scaramuzzino; M. Zarrelli | **Composites Science and Technology** |

| | Conferences, Workshops | |
|---|---|---|
| **1** | MCM2010 - XVI International Conference – Mechanics of Composites Materials<br>A comparison of model predictions and experimental characterization of NCF mechanical properties<br>Petriccione A., Annicchiarico D., Zarrelli M., Antonucci V., Giordano M. | **Riga (Lettonia)** |
| **2** | 14TH EUROPEAN CONFERENCE ON COMPOSITE MATERIALS<br>Modelling Non-Crimp fabric reinforced composite by a stiffness volume averaging approach<br>Petriccione A., Annicchiarico D., Zarrelli M., Antonucci V., Giordano M. | **Budapest, Hungary** |
| **3** | ADVANCES IN POLYMER BASED MATERIALS AND RELATED TECHNOLOGIES<br>The catalytic effect of a tertiary amine and an alchidic ammonium salt in epoxy curing systems: a comparison.<br>A. Petriccione, A. Martone, M. Zarrelli, V. Antonucci, M. Giordano | **Capri (Italy)** |